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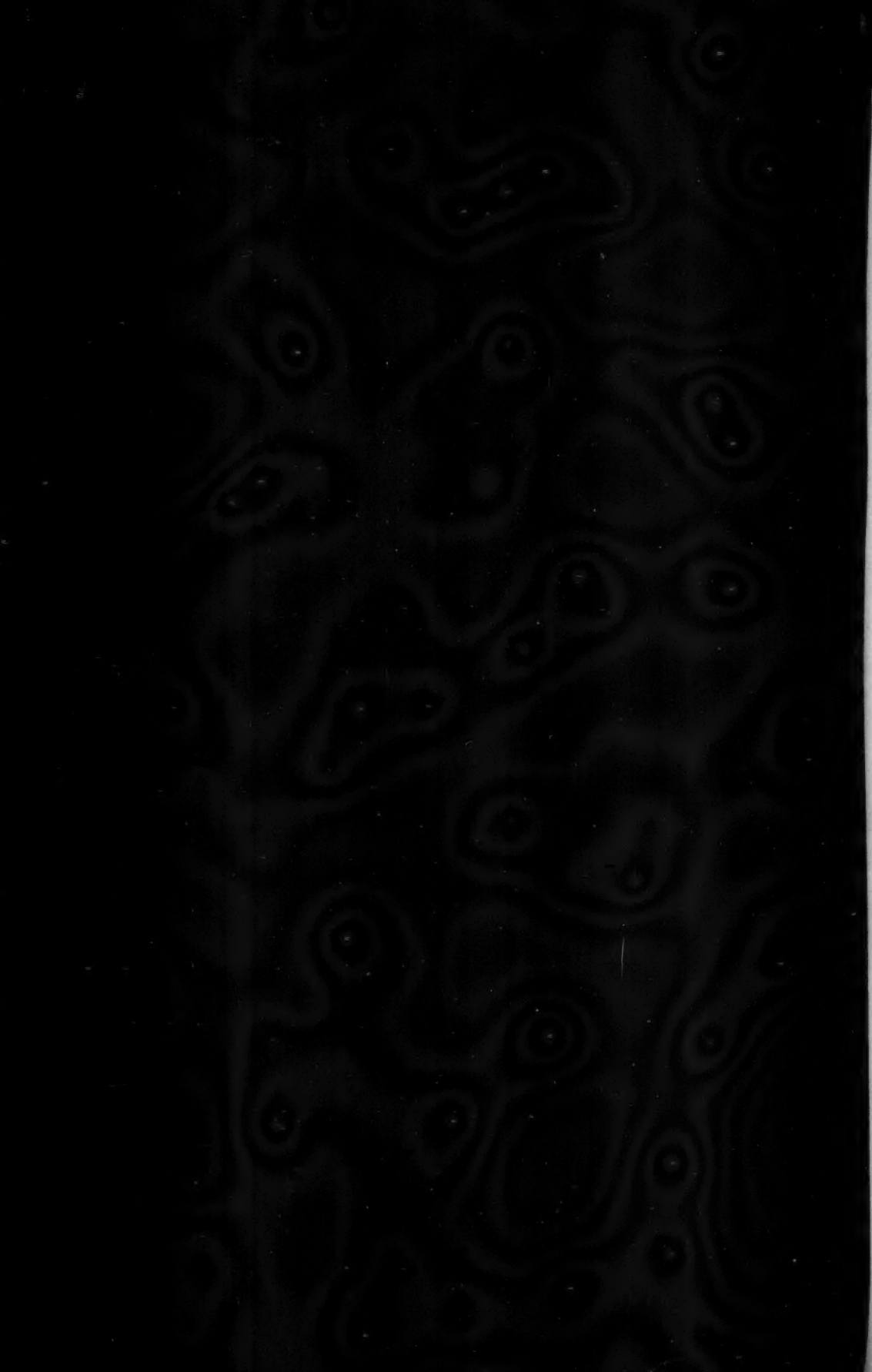


ELECTROKINETICS AND BASE-EXCHANGE CAPACITY OF SOME INORGANIC COLLOIDS

N. H. PARBERY AND SANTE MATTSON

New Jersey Experiment Station[1]

Received for publication August 7, 1931

Working with series of isoelectric precipitates of phosphates, silicates, and humates of iron and aluminum, Mattson (4) has embodied the behavior of these substances in the generalized statement, "The adsorption and exchange of cations, at pH 7.0, by soil colloids, in the same state of aggregation, increases with the increasing ratio of the acidoid to the ampholytoid constituents of the colloid." The members of these series of colloids, in which the ratio of humate, phosphate, or silicate, to iron and aluminum is greatest, are isoelectric at lowest pH, and have the largest exchange capacity. The seat of this capacity for adsorption and exchange of cations, at favorable pH ranges, lies in the free valences of the partially linked-up, yet stably combined anions.

In this work a series of isoelectric precipitates of "ferric ferrocyanide" and "sulfide of tin", and electronegative "sulfides" of antimony, bismuth, and arsenic, were prepared and their base-exchange capacities investigated.

In finding the isoelectric point of the various flocs, definite volumes of solutions A and B were measured, one into a large pyrex test tube, the other into a beaker. When required, HCl or NaOH was respectively added to the acid A, or alkaline B solutions, to give a range of pH values in the mixtures. Varying amounts of water were also added, so that the final volume of the mixtures of the same series was identical. The mixing was done by rapidly pouring one solution into the other, then back and forth between the vessels, and finally into the test tube, which was then stoppered. The flocculation immediately after the solutions were mixed, and after standing overnight, is recorded in the tables. The latter data is represented by crosses; x signifies slight, xx more complete, xxx almost complete, and xxxx complete flocculation. The pH was determined colorimetrically.

After standing overnight the tubes were shaken and cataphoretic measurements were made as described elsewhere (1).

A series of ferric ferrocyanide was prepared in which the equivalent ratios of the ferric and ferrocyanide constituents were: 15:2, 15:5, 15:10, 15:15, 15:20. By varying the pH in these series, an isoelectric compound in all but the latter

[1] This work was performed during a short visit by N. H. Parbery to New Jersey Agricultural Experiment Station. Journal Series paper of the New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology.

ratio was found. Details of this procedure together with flocculation effects, cataphoretic measurements, and pH measurements are given in systems 1–5.

It has been shown (2) that the isoelectric point of ferric hydroxide is at pH 7.1 —at or below this pH, the capacity of this compound for absorbing bases is negligible.

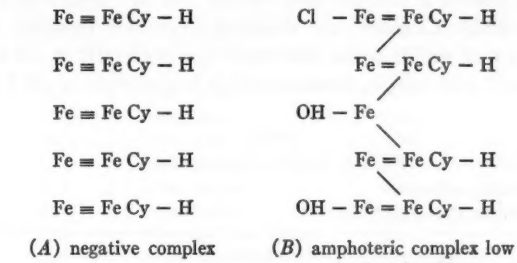
The introduction of a small amount of ferrocyanide ion into ferric hydroxide by displacement of some of the hydroxyl ion, has a marked effect in displacing the isoelectric pH of the new compound, from that of ferric hydroxide. In system 1 it will be seen that the isoelectric point is at pH 4.7. In system 2, the compound produced by the displacement of more hydroxyl ion by ferrocyanide is isoelectric at pH 4.3, and in system 3 at pH 3.9. Ferric ferrocyanide behaves then, in similar manner to the previously mentioned colloids in that, with increasing ratio of ferrocyanide to iron, the pH at the isoelectric point becomes progressively lower. The series in which stannous hydroxide is increasingly saturated with sulfide sulfur, exhibits this feature in a still more decided fashion. Both the isoelectric ferrocyanides of iron and the isoelectric sulfides of tin form natural series in which the various factors and functions vary in an ascending or descending order.

System 4 containing equivalent proportions of each constituent is isoelectric at pH 4.4 which is higher than that of system 3. The cause of this reversal, if real, has not been determined. It will be noted that instant flocculation begins in system 4 at a lower pH than in systems $3<2<1$. The descending order in respect to flocculation is therefore intact.

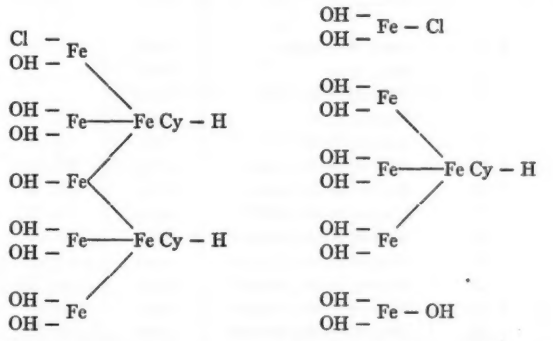
In system 5 no isoelectric point was found. Even at very low pH there was no flocculation, and feldspar particles suspended in the solutions were negatively charged. Although the ferrocyanide ion was stoichiometrically in excess of the ferric ion no ferrocyanide remained in solution when the flocculation was forced by the addition of $CaCl_2$. The flocculated electronegative complex contained no Cl ions whereas all the isoelectrically flocculated ferric ferrocyanide complexes contained appreciable quantities of Cl. The electronegative complex in system 5 might therefore be represented by formula (*A*). The Cl ions are here all displaced by the ferrocyanide and at low pH the OH ions, being greatly suppressed in the solution, would offer no competition and be practically absent in the complex. This complex must therefore remain electronegative in the first place, because of the absence of dissociable anions (e.g., Cl ions) and in the second place because of the presence of a great number of dissociable cations which exist in combination with the "free" valences of the ferrocyanide.

The other ferric-ferrocyanide complexes which all exhibit an amphoteric behavior, i.e., possess an isoelectric point, may all be represented in a general way by formulas (*B*, *C*, and *D*). These complexes contain OH and Cl as well as ferrocyanide anions. To account for the strong negative charge at the higher pH and for the cation exchange capacity (table 1b) we must assume the existence of "free" ferrocyanide valences which exist in combination with dissociable and

displaceable cations. These complexes represent therefore partly hydrolyzed salts. Since the products of the partial hydrolysis are nondiffusible and remain in the complex, the latter contains both an acid and a basic residue. In other words the complex constitutes an amphoteric colloid (5).



(*A*) negative complex (*B*) amphoteric complex low isoelectric pH



(*C*) amphoteric complex intermediate isoelectric pH (*D*) amphoteric complex high isoelectric pH

Whenever the dissociable anion (i.e., Cl) is displaced by a non-dissociable or non-diffusible anion the isoelectric pH must be displaced to the acid side: (*a*) because the dissociation of the basic group of the complex is thereby suppressed until, at a lower pH, a sufficient additional number of the OH ions of the basoid are displaced by dissociable anions, and (*b*) if the displacing anion is di- or polyvalent it will, if it forms a weak acid, only partly link itself to the basoid group, one or more of its valences remaining in combination with hydrogen or other dissociable cations. The result is a new amphoteric complex possessing: a stronger acid group, a weaker basic group, a lower isoelectric pH, a higher cation exchange capacity at a given pH on the alkaline side, and a lower anion exchange capacity at a given pH on the acid side of the isoelectric point.

STANNOUS SULFIDE

In system 6 it will be seen that the isoelectric point of stannous hydroxide, when formed from stannous chloride, is at pH 6.6.

A series of isoelectric sulfides was prepared in which there was a progressive saturation of the oxychloride of tin with sulfide sulfur. As saturation with sulfide sulfur becomes more complete, the isoelectric points of the members of the series are at increasingly low pH values. Unlike the ferrocyanide complexes, which possess a stronger acid residue and are isoelectric at low pH, sufficient dissociable Cl enters the stannous oxysulfide complex, when one-fifth saturated with sulfide sulfur, and renders it isoelectric at pH 6.2. When fully "saturated" with sulfide, stannous sulfide is isoelectric at pH 3.2.

TABLE 1

$FeCl_3$ + $Na_4[Fe(CN)_6]$—system 1

A. 7.5 m.e. $FeCl_3$ per liter.
B. 1.0 m.e. $Na_4[Fe(CN)_6]$ per liter.

SOLUTION A	SOLUTION B, 20 cc. + NaOH (1 cc. = 0.02 M.E. NaOH)*	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
20	1.5	Deep blue, none	None	.....	.....
20	2.0	Blue, none	None	.....	.....
20	3.0	Purplish blue, none	None	.....	.....
20	4.0	Purple, none	xxx	+2.16	<3.0
20	5.0	Mauve, none	xxxx	+1.51	<3.0
20	5.25	Brown-mauve, none	xxxx	+1.44	3.4
20	5.50	Brown-mauve, none	xxxx	+1.26	3.8
20	5.75	Mauve-brown, slow	xxxx	+1.21	4.1
20	5.88	Mauve-brown, rapid	xxxx	+0.87	4.4
20	6.0	Mauve-brown, instant	xxxx	+0.67	4.5
20	6.13	Mauve-brown, instant	xxxx	+0.10	4.6
20	6.18	Mauve-brown, instant	xxxx	±0.0	4.7
20	6.25	Mauve-brown, instant	xxxx	−0.15	4.8
20	6.50	Brown, instant	xxxx	−1.51	6.0
20	7.0	Brown, none	xxxx	−2.52	7.0

* Plus water to give the mixture a total volume of 50 cc.

Isoelectric mixture: {7.5 m.e. $FeCl_3$ per liter. / 1.0 m.e. $Na_4[Fe(CN)_6]$ + 6.18 m.e. NaOH in 1,500 cc.
pH 4.7.
Fe and $Fe(CN)_6$ in solution, nil.

Composition of floc: $Fe_4(OH)_{10.288}[Fe(CN)_6]_{0.4}Cl_{0.182}$.

In these formulas no allowance is made for the acid and basic residues resulting from hydrolysis as indicated in formulas (*B*, *C*, and *D*).

When sodium sulfide was added in excess of equivalent proportions to stannous chloride, flocculation did not result and acidification was necessary to bring it about. No isoelectric point of this compound was found. This is because in acid solution, and in the presence of excess sulfide ions, the anion adsorption capacity of the floc is satisfied by sulfide ions, to the exclusion of dissociable chloride ions. Thus an isoelectric or electropositive compound,

TABLE 2

$FeCl_3$ + $Na_4[Fe(CN)_6]$—system 2

A. 7.5 m.e. $FeCl_3$ per liter.
B. 2.5 m.e. $Na_4[Fe(CN)_6]$ per liter.

SOLUTION A	SOLUTION B, 20 cc. + NaOH (1 cc. = 0.02 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
20	2.5	Blue, none	xxxx	+1.59	<3.0
20	3.0	Blue, none	xxxx	+1.47	3.0
20	3.5	Blue, none	xxxx	+1.21	3.2
20	4.0	Blue, slow	xxxx	+0.86	3.6
20	4.5	Blue, instant	xxxx	+0.20	4.1
20	4.6	Blue, instant	xxxx	±0.0	4.3
20	5.0	Greenish blue, instant	xxxx	−1.26	4.8
20	5.5	Bluish green, none	None	.....	...
20	6.0	Blue-gray, none	None	.....	...
20	6.5	Gray-mauve, none	None	.....	...
20	7.0	Gray-brown, none	xx	.....	...

Isoelectric mixture: {7.5 m.e. $FeCl_3$ per liter. / 2.5 m.e. $Na_4[Fe(CN)_6]$ + 4.6 m.e. NaOH in 1,500 cc.
pH 4.3.
Fe and $Fe(CN)_6$ in solution, nil.
Composition of floc: $Fe_4(OH)_{7.84}[Fe(CN)_6]_{1.0}\ Cl_{0.16}$.

TABLE 3

$FeCl_3$ + $Na_4[Fe(CN)_6]$—system 3

A. 7.5 m.e. $FeCl_3$ per liter.
B. 5.0 m.e. $Na_4[Fe(CN)_6]$ per liter.

SOLUTION A	SOLUTION B, 20 cc. + NaOH (1 cc. = 0.01 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
20	6.0	Blue, none	None	.....	...
20	5.0	Blue, very slow	xxxx	−1.51	5.0
20	4.8	Blue, instant	xxxx	−1.21	4.6
20	4.6	Blue, instant	xxxx	−0.89	4.5
20	4.4	Blue, instant	xxxx	−0.61	4.3
20	4.2	Blue, instant	xxxx	−0.41	4.2
20	4.0	Blue, instant	xxxx	−0.22	4.1
20	3.8	Blue, instant	xxxx	− slight	4.0
20	3.6	Blue, instant	xxxx	±0.0	3.9
20	3.4	Blue, instant	xxxx	.....	3.8
20	3.2	Blue, instant	xxxx	+0.19	3.7
20	3.0	Blue, instant	xxxx	+0.30	3.6

Isoelectric mixture: {7.5 m.e. $FeCl_3$ per liter. / 5.0 m.e. $Na_4[Fe(CN)_6]$ + 1.8 m.e. NaOH in 1,500 cc.
pH 3.9.
Fe and $Fe(CN)_6$ in solution, nil.
Composition of floc: $Fe_4(OH)_{3.6}[Fe(CN)_6]_{2.0}\ Cl_{0.40}$.

except perhaps in very strongly acid solution, could not be obtained. The following formula illustrates the probable structure of this sulfide.

$$S_n = S$$

$$S \begin{cases} S_n - S - H \\ S_n - S - H \end{cases}$$

$$S_n = S$$

In preparing the series of sulfides, the amount of stannous chloride was kept constant, and varying amounts of sodium sulfide (plus varying amounts of

TABLE 4

$FeCl_3$ + $Na_4[Fe(CN)_6]$—system 4

A. 7.5 m.e. $FeCl_3$ per liter.
B. 7.5 m.e. $Na_4[Fe(CN)_6]$ per liter.

SOLUTION A	SOLUTION B, 20 cc. + NaOH (1 cc. = 0.02 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
20	7	Light brown, none	None	.....	...
20	5	Green, none	None	.....	...
20	1	Greenish blue, none	None	.....	...
SOLUTION A, 20 cc. + HCl (1 cc. = 0.01 M.E. HCl)	SOLUTION B				
cc.	*cc.*				
0.2	20	Blue, none	xxxx	−1.51	5.2
0.4	20	Blue, very slow	xxxx	−1.21	4.6
0.6	20	Blue, very slow	xxxx	±0.0	4.4
0.8	20	Blue, very slow	xxxx	+0.15	4.2
1.0	20	Blue, slow	xxxx	+0.17	4.1
1.4	20	Blue, instant	xxxx	.....	3.9
1.6	20	Blue, instant	xxxx	.....	3.8
1.8	20	Blue, rapid	xxxx	+0.17	...
5.0	20	Blue, slow	xxxx	+0.30	<3.0

Isoelectric mixture: { 7.5 m.e. $FeCl_3$ per liter.
7.5 m.e. $Na_4[Fe(CN)_6]$ + 0.3 m.e. HCl in 1,500 cc.
pH 4.4.
Fe and $Fe(CN)_6$ in solution, nil.

Composition of floc: $Fe_4[Fe(CN)_6]_3\,Cl_{0.41S}$.

HCl or NaOH to give pH ranges for each compound) were added, so as to give ratios of tin and sulfide, expressed on a milliequivalent basis of 5:1, 5:2, 5:3, 5:4, 5:5, 5:6.

As already stated, the last-mentioned ratio was the only one in which an isoelectric point was not found.

TABLE 5

$FeCl_3$ + $Na_4[Fe(CN)_6]$—system 5

A. 7.5 m.e. $FeCl_3$ per liter.

B. 10.0 m.e. $Na_4[Fe(CN)_6]$ per liter.

SOLUTION A, 20 cc. + HCl (1 cc. = 0.01 M.E. HCl)	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
2	20	Blue, none	None	.....	.....
4	20	Blue, none	None	.....	.....
6	20	Blue, none	None	.....	.....
8	20	Deeper blue, none	None*	.....	.....
10	20	Deeper blue, none	None†	.....	.....
SOLUTION A, 20 cc. + HCl (1 cc. = 0.10 M.E. HCl)					
cc.					
2	20	Deeper blue, none	None	.....	.....
3	20	Deeper blue, none	None	.....	.....
10	20	Deepest blue, none	None	.....	<3.0

* When flocculated with $CaCl_2$, floc negatively charged.

† Feldspar particles suspended in solution were negatively charged.

There is neither isoelectric point nor flocculation even at very low pH.

Complete flocculation of mixture at low pH was effected with $CaCl_2$, and no Fe or $Fe(CN)_6$ remained in solution.

TABLE 6

$SnCl_2$ + NaOH—system 6

A. 8.0 m.e. $SnCl_2$ per liter.

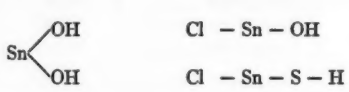
SOLUTION A	NaOH IN 25 CC. (1 CC. NaOH = 0.025 M.E.)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
25	9.0	Slight opalescence, none	None	.....	<4.0
25	10.05	Opalescence, none	x	+1.51	5.5
25	10.2	Slow	xxxx	+1.73	6.3
25	10.3	Instant	xxxx	+1.44	6.4
25	10.4	Instant	xxxx	+1.01	6.5
25	10.6	Opalescence, none	x	−0.92	6.7
25	11.0	Slight opalescence, none	x	−0.93	6.9
25	14.0	None	None	.....	>8.0

Isoelectric mixture: { 8 m.e. $SnCl_2$ per liter.
10.5 m.e. NaOH per liter.
pH 6.6.

The amount of chlorine adsorbed by the compounds at their isoelectric points was not determined, but from analogy with the behavior of ferric ferrocyanide, the lower the pH at the isoelectric point of the compound the greater will be the amount of chlorine adsorbed.

The following formulae illustrate chlorine adsorption.

The first represents stannous hydroxide, isoelectric at high pH, and therefore adsorbing a small amount of chlorine, and the second, stannous hydroxide partly saturated with sulfide ion, isoelectric at lower pH, and adsorbing more chlorine.



Stannous hydroxide, or stannous oxychloride, and the various sulfides as prepared, flocculated only over a comparatively narrow pH range. These compounds are dispersed on the acid and alkaline side of the isoelectric point. At the isoelectric point some of the higher ratio sulfides behave in unstable fashion, and the passage of electric current for a very short period will cause the particles to assume various charges. It is conceivable that a colloidal particle, partially saturated with sodium at the moment the current passes through the cataphoresis tube, undergoes electrolysis and becomes hydrogen-saturated, with an accompanying change of pH and charge.

ARSENIOUS SULFIDE

Arsenious sulfide has long been quoted as a classical example of a negative colloid.

Following the methods for the preparation of ferrocyanide series, an attempt was made to prepare a natural series in which there would be an increasing saturation of arsenious oxide with sulfide sulfur.

Definite quantities of a solution of sodium sulfide (standardized with respect to sulfide sulfur) containing 200 m.e. sulfide sulfur per liter, and a solution of arsenious oxide containing 400 m.e. As_2O_3 and 400 m.e. HCl per liter, were mixed and made up to 1 liter. The ratios of sulfur to As_2O_3 on a milliequivalent basis were: 30:25, 25:25, 20:25, 15:25, 25:25, 10:50.

In the first two mixtures flocculation was incomplete and acidification was necessary for complete precipitation. A solution of a sodium polysulfide, the composition of which approximated Na_2S_3 was standardized with respect to sulfide sulfur, and mixtures were made in liter volumes in which the ratios were 30 m.e. sulfide sulfur: 25 m.e. As_2O_3, 30:30, and 10:30. Again in the two highest ratios acidification was necessary for complete precipitation.

In all mixtures except the two cases where sulfide was in excess of arsenic, the precipitation of sulfide was complete—it combined with nearly an equivalent

TABLE 7

$SnCl_2$ + Na_2S—system 7

A. 8 m.e. $SnCl_2$ per liter.
B. 1.6 m.e. Na_2S per liter.

SOLUTION A	SOLUTION B, 25 cc. + NaOH (1 cc. = 0.025 M.E. NaOH)*	FLOCCULATION		μ/CM. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
25	7.0	None	None	.....	...
25	8.6	Slow	xxxx	+0.61	5.8
25	8.8	Instant	xxxx	±0.0	6.2
25	9.0	Instant	xxxx	−0.15	7.4
25	9.4	Slow	xxxx	−0.24	6.7
25	9.5	Very slow	Opalescent	−1.04	6.8
25	9.6	None	None	.....	6.9

* Plus water to give the mixture a total volume of 60 cc.

Isoelectric mixture: {8 m.e. $SnCl_2$ per liter. / 1.6 m.e. Na_2S + 8.8 m.e. NaOH in 1,400 cc.
pH 6.2.
Tin and sulfide in solution, nil.

Composition of floc: $Sn(OH)_{1.6-x}\ S_{0.2}\ Cl_x$.

In these formulas no allowance is made for the free acid residue which undoubtedly exists, as indicated by formula (*F*).

TABLE 8

$SnCl_2$ + Na_2S—system 8

A. 8 m.e. $SnCl_2$ per liter.
B. 3.2 m.e. Na_2S per liter.

SOLUTION A	SOLUTION B, 25 cc. + NaOH (1 cc. = 0.025 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
25	5.0	None	None	.....	...
25	7.2	Instant	xxxx	+0.61	5.8
25	7.3	Instant	xxxx	+0.38	6.1
25	7.35	Instant	xxxx	±0.0	6.2
25	7.4	Instant	xxxx	−0.76	6.2
25	7.5	Instant	xxxx	.....	6.4
25	8.0	None	None	.....	...

Isoelectric mixture: {8 m.e. $SnCl_2$ per liter. / 3.2 m.e. Na_2S + 7.35 m.e. NaOH in 1,400 cc.
pH 6.2.
Tin and sulfide in solution, nil.

Composition of floc: $Sn(OH)_{1.2-x}\ S_{0.4}\ Cl_x$.

amount of As_2O_3 and an approximate stoichiometric As_2S_3 was formed. Where arsenic was in excess, nearly the estimated excess remained in solution.

TABLE 9

$SnCl_2$ + Na_2S—system 9

A. 8.0 m.e. $SnCl_2$ per liter.
B. 4.8 m.e. Na_2S per liter.

SOLUTION A	SOLUTION B, 25 cc. + NaOH (1 cc. = 0.025 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
25	3.0	None	None	.....	...
25	5.3	Instant	xxxx	+0.43	4.6
25	5.4	Instant	xxxx	±0.0	5.2
25	5.5	Instant	xxxx	−0.24	5.4
25	5.6	Instant	xxxx	−0.40	5.6
25	6.5	None	None	.....	...

Isoelectric mixture: {8.9 m.e. $SnCl_2$ per liter. / 4.8 m.e. Na_2S + 5.4 m.e. NaOH in 1,400 cc.
pH 5.2.
Tin and sulfide in solution, nil.
Composition of floc: $Sn(OH)_{0.8-x}S_{0.6}\ Cl_x$.

TABLE 10

$SnCl_2$ + Na_2S—system 10

A. 8.0 m.e. $SnCl_2$ per liter.
B. 6.4 m.e. Na_2S per liter.

SOLUTION A	SOLUTION B, 25 cc. + NaOH (1 cc. = 0.025 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
25	2.0	Instant	xxxx	+0.76	...
25	3.65	Instant	xxxx	+0.38	4.0
25	3.70	Instant	xxxx	+0.30	4.1
25	3.75	Instant	xxxx	±0.0*	4.3
25	3.8	Instant	xxxx	−slight	4.4
25	4.0	Instant	xxxx	−0.60	4.6

* Particles behave indefinitely, becoming variously charged as a result of electrolysis.

Isoelectric mixture: {8.0 m.e. $SnCl_2$ per liter. / 6.4 m.e. Na_2S + 3.75 m.e. NaOH in 1,400 cc.
pH 4.3.
Tin and sulfide in solution, nil.
Composition of floc: $Sn(OH)_{0.4-x}S_{0.8}\ Cl_x$.

The composition of sulfides of arsenic approaches more closely a stoichiometric relationship in the less acid mixtures. The fact that in the most acid solutions the composition departs farthest from theoretical proportions, can be explained

by the fact that, apart from solubility effects, there would be a greater tendency in the more acid solutions for adsorption by the compounds of sulfide anion. Thus arsenious sulfide itself adsorbs sulfide ions in acid solution and so an excess of sulfide appears to combine with its equivalent of As_2O_3. Cataphoretic studies were made of all the sulfides, and without exception, even at low pH, they were strongly electronegative. The excess of HCl in the more

TABLE 11

$SnCl_2$ + Na_2S—system 11

A. 8 m.e. $SnCl_2$ per liter.
B. 8 m.e. Na_2S per liter.

SOLUTION A	SOLUTION B, 25 CC. NaOH (1 CC. = 0.025 M.E. NaOH)	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
25	0.4	Instant	xxxx	+0.20	3.0
25	0.5	Instant	xxxx	±0.0	3.2
25	0.6	Instant	xxxx	−0.28	...
25	0.7	Instant	xxxx	−0.40	...
25	3.0	None	None	.....	4.4

Isoelectric mixture: { 8 m.e. $SnCl_2$ per liter. / 8 m.e. Na_2S + 0.5 m.e. NaOH in 1,400 cc.

TABLE 12

The composition of arsenious sulfide formed under various conditions

RATIO OF S TO As_2O_3	FROM SODIUM SULFIDE	FROM SODIUM POLYSULFIDE
m.e.		
25:25	$As_{1.892}\ S_3$	
20:25	$As_{1.901}\ S_3$	
15:25	$As_{1.880}\ S_3$	
10:25	$As_{1.898}\ S_3$	
10:50	$As_{1.830}\ S_3$	
30:30		$As_{1.980}\ S_3$
10:30		$As_{1.854}\ S_3$

acid mixtures interfered with cataphoretic determinations, and dilutions had to be made.

Suspensions of arsenious oxide in water are electronegative. In dilute HCl it is also electronegative, though it was thought that the momentary attachment of chloride ions to the As_2O_3 particle during its solution, and the consequent dissociation of chloride ions ($As_2{}^+O_2Cl + Cl^-$) might render the compound positive. It appears, however, that the attachment of the chloride ion results in an immediately soluble product. The oxide in water is acidic and dissociates diffusible cations, and so renders the oxide electronegative.

$$H_2 A_s O_3 + H^+$$

Arsenic appears to be too acidic (like phosphorus) to exist as a colloidal cation such as iron, tin, antimony, and other distinctly metallic elements.

ANTIMONY SULFIDE

In the case of the metals iron and tin, the oxychlorides are isoelectric at pH 7.1 and 6.6 respectively. The oxychloride of antimony is isoelectric at pH 5.6,

TABLE 13

$SbCl_3$ + NaOH—system 12

A. 2,000 m.e. $SbCl_3$ per liter.

SOLUTION A (1 CC. = 2.0 M.E. $SbCl_3$)	NaOH (1 CC. = 0.2 M.E. NaOH) MADE UP TO 599 CC.	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
1	25.90	Instant	xxxx	+1.01	4.3
1	25.95	Instant	xxxx	+0.82	4.8
1	26.00	Instant	xxxx	+0.64	5.4
1	26.05	Instant	xxxx	±0.0	5.6
1	26.30	Instant	xxxx	−1.01	5.8
1	26.80	Instant	xxxx	−1.01	6.4
1	26.90	Instant	xxxx	−0.92	6.8
1	27.00	Instant	xxxx	−0.76	7.0
1	27.30	Instant	xxxx	−1.01	7.2

Isoelectric mixture: 2 m.e. $SbCl_3$ + 5.21 m.e. NaOH in 600 cc. pH 5.6.

TABLE 14

$SbCl_3$ + Na_2S—system 13

A. 2,000 m.e. $SbCl_3$ per liter.
B. 1.6 m.e. Na_2S per liter.

SOLUTION A (1 CC. = 2.0 M.E. $SbCl_3$)	NaOH (1 CC. = 0.2 M.E. NaOH) ADDED TO 250 CC. SOLUTION B, AND DILUTED TO 599 CC.	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
1	20.0	Instant	xxxx	−2.33	<3.0
1	21.2	Instant	xxxx	.....	<3.0
1	22.8	Instant	xxxx	−2.53	3.4
1	23.0	Instant	xxxx	−2.43	3.6
1	23.2	Instant	xxxx	−1.38	3.8
1	23.4	Instant	xxxx	−2.02	4.0

No isoelectric point was found even at low pH.

and differs from that of iron and tin in that it contains much more chlorine at the isoelectric point, and its chlorine is in a much more rigidly associated condition. It will be seen that despite the high chlorine content of the oxychloride of antimony, a comparatively low pH is necessary for the complex to yield dis-

sociable chloride ions. Difficulty was experienced with solutions of S_bCl_3, which can only be kept molecularly dispersed in strong HCl solutions. An aqueous solution containing 8 m.e. S_bCl_3 per liter could not be made up and it was necessary to make up a solution containing 2,000 m.e. S_bCl_3 per liter, take 1 cc. of this solution on a watch glass and plunge it into a large volume of water + NaOH, or NaOH + Na_2S, in the preparation of the series, to prevent its premature hydrolysis.

A natural series of isoelectric sulfides of antimony, as prepared in the case of tin, cannot be prepared.

Compounds were prepared in which the ratios of antimony to sulfide sulfur on a milliequivalent basis were: 5:1, 5:2, 5:3. All these compounds were electronegative in the pH ranges examined. They could not be examined in very acid solutions because the evolution of gas at the electrodes prevented cataphoretic measurements.

TABLE 15

$BiCl_3$ + NaOH—system 14

A. 2,000 m.e. $BiCl_3$ per liter.

SOLUTION A (1 CC. = 2.0 M.E. $SbCl_3$)	NaOH (1 CC. = 0.2 M.E. NaOH) IN 599 CC. SOLUTION	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		On mixing	Overnight		
cc.	*cc.*				
1	8	Instant	xxxx	−slight	2.8
1	12	Instant	xxxx	−slight	3.2
1	14	Instant	xxxx	−0.76	3.6
1	15	Instant	xxxx	−slight	4.5
1	16	Instant	xxxx	−1.38	5.8

No isoelectric point was found even at low pH.

It was not ascertained whether the sulfide ion displaced the oxygen or chlorine of the oxychloride, but the entry of a small amount of sulfide, as in system 13, suffices to inhibit the compound from dissociating anions, even at low pH ranges.

BISMUTH OXYCHLORIDE

In bismuth oxychloride, the extreme condition is met among the metals under review, in that there is no isoelectric point for this compound in as acid solutions as examination was possible. In preparing the oxychloride, similar methods to that adopted in the preparation of antimony oxychloride were adopted, because of the readiness with which B_iCl_3 hydrolyzes. The chloride portion of the compound is extremely rigidly held, as no anions appear to be dissociated in acid solution, and the oxychloride is strictly electronegatively charged.

Sulfides of bismuth were prepared and their base exchange properties deter-

mined, but they were not examined cataphoretically. It can fairly be assumed, however, from the behavior of the sulfides of antimony that bismuth oxychloride saturated in any degree by sulfide ion, would be electronegatively charged.

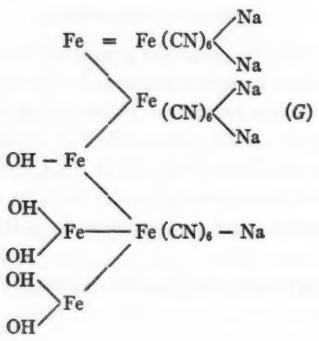
BASE EXCHANGE CAPACITY

After the isoelectric point of the various compounds had been determined, a large volume of each of the reagents was mixed in exactly the same proportions obtaining at the isoelectric point. These mixtures are given with each system where an isoelectric point was determined.

The mixtures in which ferrocyanide was in excess of iron (system 5); sulfide in excess of tin; and the sulfides of arsenic, antimony, and bismuth were all prepared in solutions made acid with HCl, for the isoelectric point of all these compounds, if existent, would be found in acid solution. The base exchange capacity of a substance is here regarded as the amount of exchangeable cation which a substance is capable of adsorbing at pH 7.

Cationic adsorption is brought about by a combination of bases with the acidic constituent of colloids. Cationic adsorption is most in evidence at high pH values—such are necessary to produce hydrolysis, by which process OH ions displace some of the valences of the acidoid component. The acidoid component is not itself displaced, however, but the number of its linkages with the basic constituent is reduced, and it must satisfy its valence requirements by linking up with cations in solution. The seat of cation adsorption and exchange reactions lies in the free valences of these partially linked-up, yet stably combined anions. It will be seen that in the ferric ferrocyanides, in which the ratio of acidoid to basoid is highest, the adsorption of cations is greatest. In these compounds there is the greatest degree of hydrolysis, which means that a larger molar fraction of the acidoid constituent is free to enter into exchange reactions.

The following formula, although not meant to represent what happens in any one molecule of ferric ferrocyanide, illustrates a high degree of hydrolysis of that compound with an accompanying high potential capacity for cation adsorption, represented by sodium ions.



(G)

The precipitates were filtered, dried at 60°C., and where sufficient material was available, about 1 gm. of the finely divided substance was used. This material was treated overnight with 50 cc. neutral *N*Ba—acetate in stoppered flasks, and then leached on the filter with *N*Ba—acetate solution adjusted to pH 7, until the filtrate had a neutral reaction. Leaching was continued somewhat further, 10 cc. *N* $BaCl_2$ adjusted to pH 7 was added, and the material washed entirely free of chloride ions with cooled boiled water. The adsorbed barium was then displaced with *N* NH_4Cl solution at 70°C. and determined as $BaSO_4$.

The base exchange capacity of the ferrocyanides was first determined by treating them by similar methods to the above, but with neutral *N* Ca-acetate. At this pH very considerable hydrolysis of the higher ratio compounds took place, and the competition of OH and acetate ions resulted in the removal of much $Fe(CN)_6$ ion, and the formation of a more basic compound, with a considerably lower exchange capacity. In all but the lowest ratio compound,

TABLE 16

Cation exchange capacities of ferric ferrocyanides at various pH values, expressed in milliequivalents per gram of material

RATIO OF IRON TO FERROCYANIDE	NORMAL SALT TREATMENT		
	Ca-acetate, pH 7	Ba-acetate, pH 6.2	Ba-acetate, pH 5.5
	m.e.		
15:2	0.380	0.428	0.046
15:5	0.334	0.563	0.051
15:10	0.426	0.678	0.092
15:15	0.421	0.971	0.384
15:20	0.450	0.677	0.557

which was comparatively stable, it was found difficult to bring the filtrate back to pH 7. The extent of the hydrolysis is reflected in the base exchange figures—all the compounds have a similar capacity for exchange, since the acidoid portion of the higher ratio compounds, which is responsible for the exchange phenomenon, has been largely lost. In washing free of Ca-acetate, there was a considerable hydrolysis of the calcium adsorbed by the higher ratio compounds. When washing was complete calcium was still being lost from these compounds but the most basic compounds were not losing calcium by hydrolysis.

Fresh samples of these compounds were treated with *N* Ba-acetate, since barium has a higher adsorption energy than calcium. In one experiment *N* Ba-acetate was adjusted to pH 6.2 with acetic acid, and in another to pH 5.5. At pH 6.2 all compounds but the highest ratio one were stable, and this compound proved stable at pH 5.5. With the exception of this compound, the base exchange capacities of the ferrocyanides of iron at pH 6.2 increase with the in-

creasing ratio of the acidoid to the ampholytoid component. At pH 5.5, where all compounds are stable, this feature, which is common to many colloids studied, is more strikingly illustrated. The base exchange capacity varies from 0.557 m.e. per gram in the highest ratio compound to 0.046 m.e. per gram in the lowest ratio.

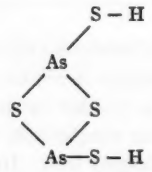
The sulfides of arsenic prepared from Na_2S and sodium polysulfide, all possess a moderate base exchange capacity when treated with Ba-acetate at pH 7. In acid solution there appears to be a certain degree of adsorption of sulfide by

TABLE 17

Cation exchange capacities of arsenious sulfides, expressed in milliequivalents per gram of material

RATIO OF SULFIDE TO As_2O_3		MILLIEQUIVALENTS PER GRAM
Using sodium sulfide	Using sodium polysulfide	
m.e.	*m.e.*	
30:25	.....	0.283
25:25	.....	0.268
20:25	.....	0.253
15:25	.....	0.247
10.25	.....	0.278
10:50	.....	0.260
.....	30:25	0.180
.....	30:30	0.216
.....	10:30	0.360

arsenious sulfide, in which case some of the valences of the sulfide component are free to link up with cations.



(*H*)

Sulfides of tin, in which there is a high ratio of sulfide to tin, have a high base exchange capacity at pH 7. It is, in effect, higher than that shown by most inorganic soil colloids which have a high SiO_2/R_2O_3 ratio.

Stannous hydroxide exhibits an appreciable base exchange capacity. When the hydroxide is one-fifth saturated with sulfide ion, this capacity rises from 0.408 m.e. per gram $Sn(OH)_2$ to 0.617 m.e. per gram in the sulfide compound.

Like the highest ratio compounds of ferric ferrocyanide, the highest ratio compounds of stannous sulfide are partially decomposed by hydrolysis at pH 7, hence the two highest ratio compounds which hydrolyze most, have their exchange capacities diminished. Had leaching with Ba-acetate been carried out

at a lower pH, the base exchange capacity would undoubtedly have increased with the increasing ratio of sulfide to tin, in a more decided manner.

The sulfides of antimony and bismuth have small base exchange capacities, indicating that at pH 7 there is little hydrolysis of these compounds, with ensuing free valences for linking with cations in solution. In the case of antimony sulfide, there is greater base exchange capacity with increasing saturation of the oxychloride with sulfide, but with bismuth sulfide the base exchange capacities are too small to be significant.

TABLE 18

Cation exchange capacities of stannous sulfides, expressed in milliequivalents per gram of material

RATIO OF TIN TO SULFIDE	MILLIEQUIVALENTS PER GRAM
m.e.	
8:9.6	0.818
8:8.0	0.810
8:6.4	0.951
8:4.8	0.897
8:3.2	0.884
8:1.6	0.617
Isoelectric stannous hydroxide	0.408

TABLE 19

Cation exchange capacity of antimony and bismuth sulfides, expressed in milliequivalents per gram of material

RATIO OF Sb TO S	RATIO OF Bi TO S	MILLIEQUIVALENTS PER GRAM
m.e.	*m.e.*	
16:16	.....	0.13
16: 9.6	.....	0.089
16: 3.2	.....	0.040
.....	16:16	0.051
.....	16: 9.6	0.036
.....	16: 3.2	0.048

GENERAL DISCUSSION

Although the ferric ferrocyanide complex formation and behavior are in general governed by the same principles as the formation and behavior of the amphoteric phosphated, silicated, humated, and proteinated (6) complexes of iron and aluminum, yet they differ from the latter in many ways: (a) All the ferrocyanide, even a certain equivalent excess, is carried down in the precipitate. (b) Small amounts of ferrocyanide cause a great downward displacement of the isoelectric pH of the ferric complex. (c) Except in system 1 there are no colloidal dispersion on the positive side even at low pH and no

ionic dispersion, i.e., solution. (d) At no very high pH (below the neutral point) is the hydrolysis extensive.

These facts taken together might help us to explain the behavior of this series. The ready hydrolysis, i.e., the ease with which the OH ions displace ferrocyanide ions, shows that the solubility product of the ferric ferrocyanide is relatively high. The fact that the compounds in system 1 and the succeeding ferric ferrocyanide systems are isoelectric at low, and not greatly differing, pH values can therefore not be due to a complete association of the ferrocyanide ions, thus preventing the entrance of dissociable Cl ions. The Cl ions are present in these complexes in greater number than were found in the isoelectric "silicates." The low isoelectric points of the ferric ferrocyanides must be ascribed to the fairly strong acid residue of the ferrocyanide group. This means a high cation dissociation even at low pH. More dissociable Cl is therefore required to render the complex isoelectric, hence the low isoelectric points.

An amphoteric colloid having a strong acid residue must have a correspondingly weaker basic residue because the neutralization must proceed until the product of the H and OH ions equals the ion product of water. The isoelectric pH must then be far below the neutral point because only at such low pH will the dissociation of the weak basoid group balance that of the acidoid group.

Stannous "hydroxide" or oxychloride is isoelectric at about pH 6.6. It has therefore somewhat stronger acidic than basic properties. This accounts for the considerable adsorption and exchange of cations at pH 7. Iron and aluminum "hydroxides" are isoelectric when precipitated from the chlorides by NaOH at about 7.1 and 8.1 respectively. None of these adsorb or exchange cations at the neutral point, but they adsorb large quantities of bases from alkaline solutions. These are therefore stronger as basoids than as acidoids(2).

When the sulfide ions displace the dissociable Cl ions the isoelectric pH is displaced to the acid side: (*a*) because the anionic dissociation of the complex is suppressed and (*b*) because the $-SH$ group introduces a stronger acid residue and thus increases the content and dissociation of diffusible cations. The cation exchange capacity is therefore greater in the sulfide complex.

Let us now briefly consider the three members of the same group; namely, arsenic, antimony, and bismuth.

Arsenic oxide is mainly acidic but the fact that it forms a chloride shows it to be amphoteric. If the compound remained insoluble its particles would undoubtedly be found to have an isoelectric point and to become electropositive at very low pH, since the acidic properties of arsenic are much stronger than the basic. But solution results, and the positive complex resolves itself into single (or an approach to single) ions such as $As_2O_2^{++}$, AsO^+, and As^{+++} and is no longer within the domain of the colloid chemist. The same would be true of of Al and Fe if the isoelectric pH of their hydroxides were below the point of true solution. No positive sols of aluminum and iron hydroxides would then be known.

The fact that arsenious oxide and especially the oxychloride are quite soluble accounts for the uniform composition of the precipitates of the various arsenious sulfide systems and for the nearly constant exchange capacities of these compounds. The formation of a natural series as in the various other systems cannot here take place. Displaceable hydrogen as indicated in formula (*H*) must, however, be assumed.

The oxychloride of antimony is isoelectric at pH 5.6 and is therefore more acidic or less basic than tin but more basic than arsenic. Being considerable stronger as an acidoid than as a basoid, its electropositive and basic properties are completely suppressed by the entrance of small amounts of sulfide ions into the complex. All of the antimony sulfide complexes are therefore negative down to the lowest pH values investigated.

The low exchange capacities of the various electronegative "sulfides" indicate a weak acidoid or a small acid residue. But it must be pointed out that the ion exchange capacity as determined by leaching is never a good criterion since one never knows how far the hydrolysis proceeds.

Bismuth is the most basic element of the three members of the group and we should expect the oxychloride to be isoelectric at a higher pH than the corresponding compound of antimony. The fact that the oxychloride of bismuth is electronegative over the entire range of pH may be due to the Cl ions not being dissociated by the complex. We have selected the Na and Cl ions as the diffusible ions which are most likely to be highly dissociated by the colloidal complexes. Where this is not the case we shall encounter irregularities. Thus in the case of silver chloride, HCl or any other chloride will cause a negative charge (6).

While a positive charge appears to be associated solely with basic materials which combine with acids and dissociate diffusible anions, a negative charge is no indication that the material is an acidoid. All inert substances such as collodion, air bubbles, etc., charge themselves negative in water. This must be a property of the water itself due perhaps to the orientation of the interfacial layer of molecules and to an unequal distribution of the OH and H ions at the phase boundary. The positive charge resulting from the dissociation of anions is therefore not only opposed by the negative charge resulting from the dissociation of cations but also by a certin phase boundary potential. The isoelectric point may therefore not represent that pH at which the dissociation of anions and that of cations are equal, but a somewhat lower pH.

SUMMARY

A series of isoelectric precipitates of "ferric ferrocyanide" and "sulfide of tin" and electronegative "sulfides" of antimony, bismuth, and arsenic, were prepared and their base adsorption and exchange capacities determined.

Details of the method of preparation of the isoelectric compounds, together with flocculation effects, cataphoretic and pH measurements are given.

The introduction of the ferrocyanide ion in increasing amounts into the

oxychloride of iron, results in compounds whose isoelectric points are at low ranges.

Arsenious sulfide is strictly electronegative, and formed under different conditions, its composition always closely approaches a stoichiometric relationship. Arsenic appears to be too acidic to exist as a colloidal cation like the distinctly metallic elements.

A series of isoelectric sulfides of tin, in which the proportion of sulfide and base varied, showed that the isoelectric points of the compounds were at lower pH values, as the compounds became more saturated with sulfide sulfur. When sulfide is in excess of tin, as when ferrocyanide is in excess of iron, no isoelectric point for the compound exists.

The isoelectric point of antimony oxychloride is at a comparatively low pH, despite the high content of chlorine at the isoelectric point. This chlorine appears to be very slightly dissociated. All sulfides of antimony are electronegative.

Bismuth oxychloride represents the extreme condition among the metals under review, in that it has no isoelectric point, being electronegative over a wide pH range.

The base exchange capacity of the ferric ferrocyanides, at a pH where the higher ratio compounds did not decompose, was found to increase with the increasing ratio of the acidoid to the ampholytoid component. The same phenomenon was found in the sulfides of tin and antimony. Arsenious sulfide has a moderate exchange capacity at pH 7, that of the sulfides of bismuth being slight. Further investigations of this type into the behavior of all the metallic elements of the periodic system should bring out some interesting relationships. Work in this direction is now in progress at this institution.

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EQUILIBRIA OF THE BASE-EXCHANGE REACTIONS OF BENTONITES, PERMUTITES, SOIL COLLOIDS, AND ZEOLITES[1]

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It is exceedingly difficult to make accurate base-exchange measurements on soils because of their extreme heterogeneity. This fact has led to the study of the simpler base-exchange substances as a substitute for soil material. Many investigators have studied the synthetic material, called "permutite," under the impression that the results thus obtained would in some measure be applicable to the base-exchange phenomenon of soils. Some soil workers refer to the exchange-complex of soils as "zeolites" or "zeolitic substances." Before any results of experimental studies on permutites, zeolites, or any other base-exchange material can be applied appropriately to soils it must be shown that their identity is complete. It is the purpose of this paper to present, in a summarized manner, a comparison of some of the properties of the four main types of hydrated alumino-silicate base-exchange substances: bentonites, permutites, soil colloids, and zeolites; and to present in detail the preliminary results of the author's attempts at investigating the physical chemistry of the base-exchange reaction for representatives of these substances.

In a recent paper, Kelley, Dore, and Brown (4) present the results of some comparative studies of these base-exchange substances. Their results summarized briefly are:

> The colloidal material of soils and of bentonites contains alkali and alkali-earth bases that are not replaceable, whereas the bases in permutites and moderately ground zeolites are practically completely replaceable. The non-exchangeable bases in bentonites are either magnesium alone, or magnesium and potassium; in soil colloids they are mainly magnesium with some potassium. By prolonged grinding in the ball-mill these non-replaceable bases become exchangeable. Prolonged heating at a temperature of 350°C. does not appreciably lower the exchange capacity of either soil colloids or of bentonites; whereas that of ground natrolite was reduced to 46 per cent, that of stilbite to 7 per cent, and that of scolecite to 6 per cent of the original exchange capacities. X-ray examination showed that permutites are devoid of sufficient crystal structure to give a pattern by the Debye-Scherer method, and that none of the zeolites and feldspars examined gave an X-ray pattern having any resemblance to those of soil colloids. The X-ray patterns of soil colloids were like those of certain of the bentonites. These X-ray results are substantiated by those of Hendricks and Fry (2).

In addition to the findings of Kelley, Dore, and Brown, there are other points of similarity and differences which should be kept in mind. The colloidal

[1] Paper No. 247, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California.

properties of bentonites are very similar to those of soil colloids, the calcium-saturated forms being granular and capable of settling out of water. The sodium-saturated forms are highly dispersed in water and on the addition of an electrolyte coagulate to a flocculent mass. The behavior in water of those permutites prepared and studied in this laboratory, is practically uninfluenced by the nature of the exchangeable cation; the sodium-saturated permutites lack the high degree of dispersion in water that bentonites and soil colloids possess. Soil colloids and bentonites are remarkably stable toward dilute acids and alkalies, whereas permutites are easily decomposed by dilute acids and alkalies; and zeolites are also decidedly unstable. A large proportion of both the replaceable and non-replaceable bases of bentonites and soil colloids consists of magnesium; and by simple leaching with a solution of a magnesium salt, bentonites and soil colloids can be prepared with magnesium as the only replaceable base present. In contrast to this, no magnesium-zeolites have as yet been reported; and hitherto it has not been possible to prepare a permutite with more than 50 per cent of the replaceable bases as magnesium, by leaching with magnesium-salt solutions.

It does not seem likely that all these differences between soil colloids and bentonites on the one hand and permutites and zeolites on the other are caused by a mere difference in crystal structure. Yet there is a remote possibility that bentonites, permutites, and zeolites are only different crystalline modifications of the same fundamental substance, for they are all hydrated alumino-silicates of fairly similar composition; and it is conceivable that they may all behave similarly as regards the base-exchange reaction. Comparatively little study has been made of the physical chemistry of the cation-exchange reaction. Kerr (5) has investigated the calcium-magnesium exchange reactions of bentonites, permutites, soils, and natural zeolites. His conclusions are that soils and bentonites are very similar, and that zeolites and permutites differ from soils. The writer has been investigating the physical chemistry of the cation-exchange reaction for some representatives of the four principal types of hydrated alumino-silicates, the preliminary results being presented in this paper.

THEORETICAL

The reaction between a solution of potassium chloride and a sodium-saturated base-exchange substance can be represented by the equation

$$NaZ + K^+ = KZ + NA^+,$$

where Z symbolizes the complex anion of the substance. When this system is given sufficient time to attain equilibrium the conditions of the system are expressed by the equation:

$$\frac{(KZ)}{(NaZ)} \times \frac{(Na^+)}{(K^+)} = K \qquad (A)$$

In which K is the equilibrium constant, and all the quantities in parentheses are the activities (7, chap. 22) of the four constituents of the reaction. These activities, or active concentrations, must not be confused with the actual or stoichiometric concentrations. But where, as in this experimental work, the solutions are fairly dilute and of nearly constant ionic strength (7, p. 373) we can use the actual stoichiometric concentrations of sodium and potassium in solution, since the activity coefficients (7, Chap. 28) of sodium chloride and potassium chloride in dilute solutions are nearly equal. Any pure solid taking part in a chemical reaction has an activity equal to unity. For example, in the reaction.

$$BaCO_3 + SO_4^{=} = BaSO_4 + CO_3^{=}$$

the equilibrium conditions are expressed by the relationship

$$K = \frac{CO_3^{=}}{SO_4^{=}}$$

because the $BaSO_4$ and the $BaCO_3$ are present as independent solid phases and the amount present is without influence. Assuming the NaZ and KZ to act like two independently existing solid phases, equation A reduces to

$$\frac{Na^+}{K^+} = K \qquad (B)$$

Kerr (5) has shown that for the calcium-magnesium exchange reaction this equation does not represent even approximately the facts for any of the base-exchange substances which he investigated. My work on the sodium-potassium, calcium-ammonium, and potassium-ammonium exchange reactions confirms his results; so this simple hypothesis may be dismissed.

Kerr (5) has advanced the idea of equating the active mass with the actual amount present in each form. Thus equation A becomes

$$\frac{KZ}{NaZ} \times \frac{Na^+}{K^+} = K \qquad (C)$$

But it must be noted that in equating active with actual concentration the tacit assumptions are made that the two substances NaZ and KZ behave as if in true solution and have the same activity coefficients. The author finds it exceedingly difficult to subscribe to this idea and prefers an entirely different viewpoint. If the NaZ and KZ are capable of forming a continuous series of mixed crystals their activities would no longer be unity. Whenever a substance in a mixed crystal enters into a chemical reaction its activity is not unity but is equal to its molecular fraction in the mixed crystal. Thus the activities of the NaZ and KZ would be given by the equations

$$(NaZ) = \frac{NaZ}{NaZ + KZ}$$

and

$$(KZ) = \frac{KZ}{NaZ + KZ}$$

respectively. Substitution of these values into equation A leads to the same equation C derived on the basis of Kerr's idea.

Thus far we have assumed that the complex anion, Z, is monobasic. Considering it to be divalent, the reaction would be represented by the expression

$$Na_2Z + 2\,K^+ = K_2Z + 2\,Na^+,$$

and the equation representing equilibria conditions, for both the mixed crystal hypothesis and Kerr's idea, would be

$$\frac{K_2Z}{Na_2Z} \times \left(\frac{Na^+}{K^+}\right)^2 = K \qquad (D)$$

Without presenting any experimental results at this point, suffice it to say that all the data support the monobasic formula and not the dibasic. So, for the sake of brevity we shall omit any further theoretical consideration of a divalent complex anion.

The study of an exchange reaction of two cations of the same valence does not permit one to distinguish between Kerr's theoretical treatment of the two solid phases, NaZ and KZ, and the mixed crystal hypothesis. But the exchange reaction using two dissimilar cations does afford data for distinguishing between the two hypotheses. Using a solution of ammonium chloride and a calcium-saturated material the reaction is

$$2\,NH_4Z + Ca^{++} = CaZ_2 + 2\,NH_4^+,$$

and the corresponding expression for the equilibrium conditions in terms of the activities of the four constituents is

$$K = \frac{(NH_4^+)^2}{(Ca^{++})} \times \frac{(CaZ_2)}{(NH_4Z)^2} \qquad (E)$$

Here again the parentheses denote activities. Since the solutions used in this experimental work are fairly dilute and of nearly constant ionic strength the error introduced by the omission of the activity coefficients of NH_4Cl and $CaCl_2$ solutions is nearly constant for all the experiments. Assuming the particles of the substances to be so finely divided as to behave as if in solution (6), equation E becomes

$$K = \frac{NH_4^{+2}}{Ca^{++}} \times \frac{CaZ_2}{NH_4Z^2} \qquad (F)$$

If the NH_4Z and CaZ_2 form a continuous series of mixed crystals a different expression results. The activities of the two forms of the substance are given by the expressions

$$(NH_4Z) = \frac{NH_4Z}{NH_4Z + CaZ_2}$$

and

$$(CaZ_2) = \frac{CaZ_2}{NH_4Z + CaZ_2}$$

Substitution of these values into equation E results in the expression

$$K = \frac{NH_4^{+2}}{Ca^{++}} \times \frac{CaZ_2(CaZ_2 + NH_4Z)}{NH_4Z^2} \qquad (G)$$

which differs from equation F by the factor $(NH_4Z + CaZ_2)$. Thus the data obtained by a study of the equilibria of the calcium-ammonium exchange reaction should afford a means of distinguishing between the two theories as to the rôle of the solid phases.

THE MATERIALS USED AND THEIR PREPARATION

The author studied the sodium-potassium exchange reaction for the following materials: two bentonites, two permutites, two soil colloids, and two zeolites.

The colloidal fractions of the two soils were prepared by sedimentation of the sodium-saturated soil in water; only that material remaining suspended in the upper 20 cm. after a period of 24 hours was used. The suspended material was coagulated by the addition of ammonium chloride. Treatment with ammonium hydroxide solution, followed by oxidation with 5 per cent hydrogen peroxide solution served to remove practically all the organic matter. The use of hydrogen peroxide results in an acid preparation. To remove the hydrogen ions the material was treated with a dilute solution of calcium hydroxide until distinctly alkaline; then it was rendered practically neutral by continued leaching with normal ammonium chloride solution, adjusted to a pH of 6.8 to 7.0 until the ammonium chloride solution came through with its pH unaltered.

The colloidal fractions were separated from two bentonites in the same manner, except that the treatment for the removal of organic matter and the subsequent use of calcium hydroxide solution were omitted because these clays contained little if any organic matter. Bentonite 7 is of the montmorillonite type, having a silica-alumina ratio of very nearly 5 to 1. Bentonite 5 is more like the beidellite type and has a silica-alumina ratio of about 4 to 1.

The two natural zeolites, analcite and heulandite, whose compositions approximated very closely the theoretical, $Na_2O \cdot Al_2O_3 \cdot 4\ SiO_2 \cdot \times H_2O$ and $CaO \cdot$

$Al_2O_3 \cdot 6\ SiO_2 \cdot \times H_2O$ respectively, were ground rather finely before being used. They were treated by decantation with neutral normal ammonium chloride solution until most of their cations had been replaced by the ammonium ion.

Two synthetic preparations were investigated. The one, permutite 51, having a composition expressed by the formula $Na_2O \cdot Al_2O_3 \cdot 5\ SiO_2 \cdot \times H_2O$, was prepared by the addition of hot sodium aluminate solution to silicic acid suspended in boiling water. After being heated on the steam bath for a short time the product was filtered off and leached on a Buchner funnel with neutral normal sodium chloride solution until the leachate came through only slightly alkaline to phenolphthalein. It was then leached with neutral normal ammonium chloride solution until this solution came through unchanged. Permutite 31 had the composition $Na_2O \cdot Al_2\ O_3 \cdot 3\ SiO_2 \cdot \times H_2O$; it was prepared by mixing boiling hot solutions of sodium aluminate and sodium silicate. It was then treated exactly as was the other permutite.

TABLE 1

Replaceable bases in bentonites and soil colloids

(Expressed as milligram equivalents per 100 gm.)

MATERIAL	K-SATURATED FORM			Na-SATURATED FORM		
	NH_4 absorbed	Na displaced	K displaced	NH_4 absorbed	Na displaced	K displaced
Bentonite 7	99.7	0.6	97.9	109.8	108.2	0.2
Bentonite 5	86.7	0.0	89.3	93.5	92.1	0.2
Soil colloid 431	67.5	0.6	63.9	69.3	66.4	0.7
Soil colloid 5696	45.8	0.6	46.4	51.3	51.8	0.5

Each of these eight preparations was divided into two nearly equal portions after the treatment with neutral ammonium chloride solution; the one portion was leached on a Buchner funnel with neutral normal sodium chloride solution until the leachate gave no Nessler test for ammonia. The other portion was similarly treated with potassium chloride solution. The products were then freed from all but merest traces of chlorides by leaching with methyl alcohol. They were air-dried and made to pass an 80-mesh sieve.

The replaceable bases in the bentonites and soil colloids were determined by the ammonium acetate method, the absorbed ammonia being determined by aeration. The ammonium acetate leachates were analyzed for sodium and potassium only. All sodium determinations reported in this paper were made by a slight modification of the Barber-Kolthoff method (1). All the potassium determinations were made by the perchloric acid method. The results for the replaceable bases in the bentonite and soil preparations are given in table 1.

The zeolite and permutite preparations were analyzed by the standard methods, and the results are presented in table 2.

TABLE 2

Analyses of permutites and zeolites

SUBSTANCE	PER CENT		M.E. PER 100 GM.		
	SiO_2	Al_2O_3*	Na	K	Ca
Permutite 51, K form	53.64	17.83	3.5	306.8	...
Permutite 51, Na form	53.63	17.92	294.0	0.0	...
Permutite 31, K form	41.62	24.35	1.8	404.0	...
Permutite 31, Na form	44.06	25.61	421.0	0.0	...
Heulandite, K form	56.74	16.56	1.6	283.0	9.7
Heulandite, Na form	58.54	17.38	292.0	0.0	3.7
Analcite, K form†	54.75	22.72	20.0	393.0	...
Analcite, Na form	55.00	22.95	421.0	0.0	...

* These figures include the undetermined but small amounts of Fe_2O_3.

† The X-ray pattern of this potassium-saturated analcite was practically identical with that of leucite.

TABLE 3

Experimental data for bentonite 7, soil colloid 431, and permutite 51, for the sodium-potassium exchange reaction

(All concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				ANALYTICAL RESULTS					
				Bentonite 7		Soil colloid 431		Permutite 51	
Na^+	K^+	NaZ	KZ	Na^+	K^+	Na^+	K^+	Na^+	K^+
100.0	0.0	0.0	25.0	86.3	14.9	87.2	13.9	86.3	14.0
100.0	0.0	0.0	42.9	81.1	20.6	81.8	20.1	80.2	20.2
85.7	14.3	0.0	42.9	71.9	29.2	71.7	29.8	70.0	30.4
71.4	28.6	0.0	42.9	61.8	39.5	61.1	40.8	59.2	41.5
57.1	42.9	0.0	42.9	50.5	50.6	49.5	52.0	47.7	53.0
42.9	57.1	0.0	42.9	38.7	62.2	37.7	64.4	35.3	65.2
25.0	75.0	0.0	25.0	23.7	76.9	23.4	78.1	21.9	78.5
75.0	25.0	25.0	0.0	85.3	15.6	86.3	14.9	86.2	14.9
57.1	42.9	42.9	0.0	79.8	22.3	80.7	21.8	78.0	21.8
42.9	57.1	42.9	0.0	70.4	31.5	70.4	31.9	67.8	32.3
28.6	71.4	42.9	0.0	60.0	42.1	59.7	42.8	57.0	43.2
14.3	85.7	42.9	0.0	48.4	53.1	48.4	54.1	46.0	54.5
0.0	100.0	42.9	0.0	37.0	64.7	36.7	65.7	34.1	66.2
0.0	100.0	25.0	0.0	22.7	78.3	22.9	78.6	21.2	78.8

EXPERIMENTAL PROCEDURE

The sodium-potassium exchange reaction was experimentally investigated at a temperature of 25°C. and at a total concentration of tenth-normal. In order to approach equilibrium in both directions two series of experiments were

carried out simultaneously with most of the materials. In the one series various amounts of NaZ were used with 50 cc. of a tenth-normal solution containing varying ratios of sodium and potassium chlorides. In the other series of experiments corresponding amounts of KZ were used with 50 cc. of a tenth-normal solution of sodium and potassium chlorides in varying ratios. The ratio of sodium to potassium in the entire system varied from about 5:1 down to 1:5, thereby covering the composition range about as completely as the analytical accuracy permitted. The weighed amounts of material and 50 cc. of the

TABLE 4

Experimental data for heulandite, permutite 31, and soil colloid 5696

(All concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				ANALYTICAL RESULTS					
				Heulandite		Permutite 31*		Soil colloid 5696	
Na^+	K^+	NaZ	KZ	Na^+	K^+	Na^+	K^+	Na^+	K^+
100	0	0	20	90.9	8.9	87.7	11.8	90.1	10.9
100	0	0	30	88.2	11.9	83.8	15.9	87.2	14.5
100	0	0	40	85.6	14.2	80.5	19.5	84.7	17.1
100	0	0	50	83.7	16.5	77.8	22.5	82.4	19.7
80	20	0	50	69.6	30.6	63.5	36.8	68.7	33.1
70	30	0	50	62.0	38.5	56.0	44.6	61.1	41.1
50	50	0	50	45.1	55.7	40.8	60.8	44.6	57.1
40	60	0	40	37.0	63.9	33.7	67.2	36.6	64.8
30	70	0	30	27.9	72.2	26.4	74.8	28.3	72.9
20	80	0	20	19.43	81.3	18.4	82.5	19.3	81.5
80	20	20	0	90.7	9.1	86.7	13.0	89.1	11.6
70	30	30	0	87.8	12.2	81.9	17.9	86.0	15.5
60	40	40	0	84.9	14.7	77.5	21.9	83.4	18.7
50	50	50	0	82.5	17.5	74.6	25.9	80.9	21.2
30	70	50	0	69.0	31.6	60.1	40.4	67.0	35.2
20	80	50	0	61.2	39.5	52.0	47.7	59.7	42.8
0	100	50	0	44.6	56.1	37.8	64.4	43.5	58.9
0	100	40	0	36.3	63.9	31.3	69.9	35.7	65.8
0	100	30	0	27.7	72.0	24.6	76.3	27.6	73.8
0	100	20	0	19.32	81.3	17.1	83.7	18.9	81.9

* As a result of an inadvertent error, the actual amounts of sodium-saturated permutite 31 used are 2.4 per cent less than the values given.

proper sodium-potassium chloride solutions were put into pyrex test tubes, stoppered well with rubber stoppers, and left in the 25°C. thermostat from 7 to 14 days. The test tubes and contents were frequently shaken. The solutions were then filtered off and the sodium and potassium present in the filtrates were determined analytically. The experimental data showing the amounts of NaZ or KZ and the compositions of the sodium-potassium chloride solutions used, together with the analytical results, are given in tables 3, 4, and 5.

EXPERIMENTAL RESULTS AND DISCUSSION

Bentonite 7, permutite 51, and soil colloid 431 were investigated by exactly the same procedure. The initial amounts of NaZ, KZ, NaCl, and KCl were the same for all three substances; these data are given in table 3 along with the analytical results.

The proportions of the four constituents were slightly altered in the experiments with the rest of the base-exchange materials. The data for the initial

TABLE 5

Experimental data for bentonites 5 and 7, soil colloid 431, and analcite

(All concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				ANALYTICAL RESULTS							
				Bentonite 5		Bentonite 7		Soil colloid 431		Analcite	
Na^+	K^+	NaZ	KZ	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+
80	20	20	0	88.8	11.6	87.4	13.5	....	....	....	....
70	30	30	0	....	....	....	....	84.7	17.4	73.3	27.2
30	70	50	0	66.3	34.9	64.8	37.9	....	....	....	....
20	80	50	0	....	....	....	....	57.8	45.7	29.1	71.2
0	100	40	0	....	....	34.9	67.0	....	....	....	....
0	100	30	0	27.5	73.7	....	....	27.3	75.3	8.3	92.6

TABLE 6

Equilibria constants for bentonite 7 for the reaction $NaZ + K^+ = KZ + Na^+$

(Equilibrium approached from the right)

CONCENTRATIONS IN M.E. PER LITER				EQUILIBRIUM CONSTANTS		
Na^+	K^+	NaZ	KZ	Equation B	Equation C	Equation D
86.3	14.9	13.7	10.1	5.8	4.3	25.0
81.1	20.6	18.9	22.3	3.9	4.6	18.0
71.9	29.2	13.8	28.0	2.5	5.0	12.5
61.8	39.5	9.6	31.9	1.6	5.2	8.3
50.5	50.6	6.6	35.1	1.0	5.3	5.3
38.7	62.2	4.2	37.8	0.6	5.6	3.5
23.7	76.9	1.3	23.1	0.3	5.5	1.7

concentrations and the analytical results for heulandite, permutite 31, and soil colloid 5696 are given in table 4.

Only three experiments were made with bentonite 5 and with analcite; a few experiments with soil colloid 431 and bentonite 7 were repeated to arrive at some idea of the reproducibility of the results. The data for these experiments are given in table 5.

Calculations based on the data for bentonite 7, given in tables 3 and 5, are presented in tables 6 and 7. The first two columns give the analytical results for the milligram equivalents of sodium and potassium per liter of the solution.

The third and fourth columns give the calculated values for the concentrations of the NaZ and KZ as milligram equivalents per liter in the equilibria mixtures; these values are obtained by subtracting the sodium or potassium, found in the solution, from the total amounts present in the system. The figures in the fifth column are the values of the equilibrium constant K calculated according to equation B, those in the sixth column are the values for equation C, and those in the seventh column are the values for equation D. The values of the calculated equilibria constants in the fifth column of tables 6 and 7 show that the two solid forms NaZ and KZ cannot be treated like two independent solid phases. The values in columns six and seven indicate strongly that the complex-anion is monobasic rather than dibasic. The calculated values for the equilibria constants for the other substances show the same general trend.

TABLE 7

Equilibria constants for bentonite 7 for the reaction $NaZ + K^+ = KZ + Na^+$

(Equilibrium approached from the left)

CONCENTRATIONS IN M.E. PER LITER				EQUILIBRIUM CONSTANTS		
Na^+	K^+	NaZ	KZ	Equation B	Equation C	Equation D
85.3	15.6	14.7	9.3	5.5	3.5	19.3
79.8	22.3	20.2	20.6	3.6	3.6	13.0
70.4	31.5	15.3	25.6	2.2	3.7	8.1
60.0	42.1	11.4	29.3	1.4	3.7	5.2
48.4	53.1	8.7	32.6	0.9	3.4	3.0
37.0	64.7	5.9	35.3	0.6	3.4	2.0
22.7	78.3	2.3	21.7	0.3	2.7	0.8
87.4	13.5	12.6	6.5	6.5	3.3	21.0
64.8	39.7	15.2	32.1	1.6	3.6	5.9
34.9	67.0	5.1	33.0	0.5	3.4	1.8

It will be noted that the figures in column six of tables 6 and 7 give a different value for the "equilibrium constant," depending on the direction in which equilibrium is approached. The difference is such as to indicate that insufficient time was allowed for the attainment of true equilibrium. However, experimental evidence, to be presented later, points strongly to some other cause for this so-called "hysteresis." All of the materials, for which the equilibria of the sodium-potassium exchange reaction were approached in both directions, exhibited this hysteresis and approximately to the same degree.

Rather than further to burden this paper with numerous tables of calculations the results are presented graphically in figure 1. The sodium-potassium exchange reaction can be represented by the general equation

$$Na_nZ + nK^+ = K_nZ + nNa^+$$

in which n is the valence or basicity of the complex anion Z. The expression for the equilibrium constant is

$$\frac{K_nZ}{Na_nZ} \times \frac{Na^{+n}}{K^{+n}} = K$$

Rearranging the terms and taking logarithms leads to the equation

$$\log\left(\frac{NaZ}{KZ}\right) = n \log\left(\frac{Na^+}{K^+}\right) - \log K$$

This is in the form of the equation for a straight line whose slope is n, and the intercept on the axis of ordinates is the logarithm of the reaction constant K. All the experimental data for the sodium-potassium exchange reaction, in

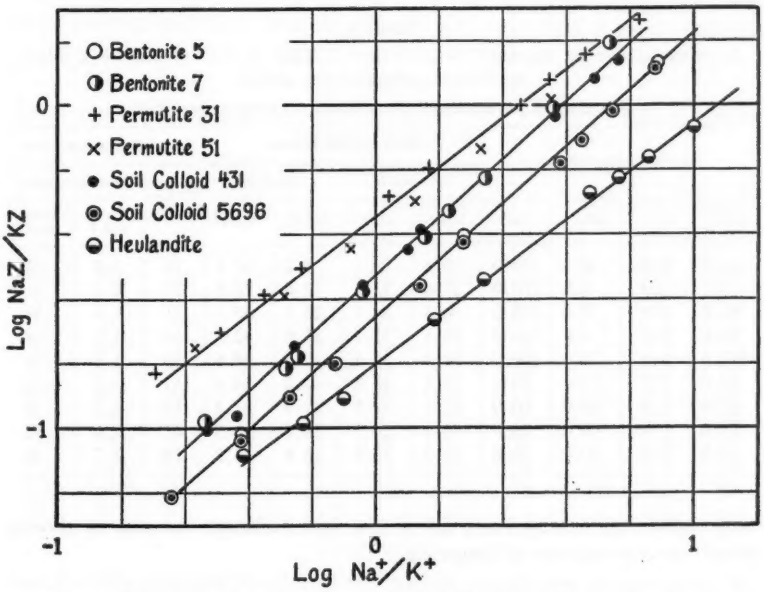

FIG. 1. EQUILIBRIA IN THE SODIUM-POTASSIUM EXCHANGE REACTION OF THE VARIOUS ALUMINO-SILICATES

which the sodium-saturated materials were used, are plotted in figure 1. The quantities $\log\left(\frac{NaZ}{KZ}\right)$ are the ordinates and $\log\left(\frac{Na^+}{K^+}\right)$ are the abscissas. The results for analcite fall outside the area of figure 1. Figure 1 shows the great similarity in behavior of soil colloid 431 and bentonite 7, and also the similarity of soil colloid 5696 and bentonite 5. The graphs for these four substances have approximately a slope of unity, indicating the monobasicity of the complex anion. It is seen that heulandite and the two permutites differ noticeably from the soil colloids and the bentonites, and that their graphs have a slope consider-

ably less than unity. This is likewise true for analcite. The apparent valency of less than one for the complex anion of the permutites and zeolites may have its origin in the incomplete validity of the assumption of a continuous series of perfect solid solutions or mixed crystals. Where, as in the case of permutites and zeolites, all of the cation is replaceable this assumption may not be valid, but may be approximately true when only one-fourth to one-third of the total cation content is replaceable. Further work is in progress regarding this point.

The results for the reverse reaction, in which the potassium-saturated materials were used, are not shown in figure 1. They form a similar set of lines all displaced to the right by about the same amount; this is because in no case was

TABLE 8

Experimental data for bentonite 7 for the reaction $2\ NH_4Z + Ca^{++} = CaZ_2 + 2\ NH_4^+$, *equilibrium approached from the left*

(Concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS		
				By analysis		Calculated		Dibasic anion	Monobasic anion	
NH_4Z	CaZ_2	NH_4^+	Ca^{++}	NH_4^+	Ca^{++}	NH_4Z	CaZ_2		Equation F	Equation G
20.0	0.0	0.0	100.0	16.8	84.3	3.2	15.7	16	5.4	55
40.0	0.0	0.0	100.0	27.4	73.2	12.6	26.8	21	1.7	44
60.0	0.0	0.0	100.0	36.3	64.7	23.7	35.3	31	1.3	54
80.0	0.0	0.0	100.0	44.1	57.7	35.9	42.3	40	1.1	63
100.0	0.0	0.0	100.0	51.0	51.4	49.0	48.6	49	1.0	73
80.0	0.0	20.0	80.0	55.8	45.4	44.2	34.6	53	1.2	74
60.0	0.0	40.0	60.0	62.1	38.7	37.9	21.3	57	1.5	73
40.0	0.0	60.0	40.0	70.9	29.5	29.1	10.5	61	2.1	72
20.0	0.0	80.0	20.0	83.2	16.8	16.8	3.2	79	4.7	86

true equilibrium attained and all of the base-exchange substances showed about the same amount of hysteresis.

INVESTIGATION OF THE RÔLE OF THE SOLID PHASE

In the theoretical section of this paper it was shown that the rôle of the solid phases in the base-exchange reaction could be ascertained only by the use of a reaction involving two cations of dissimilar valences. For this purpose, a series of experiments were performed in which bentonite 7 was used in the calcium-ammonium exchange reaction. These experiments were conducted similarly to those for the sodium-potassium reaction at a total concentration of tenth-normal and a temperature of 25° C. Two series of experiments were carried out, the one using calcium-saturated bentonite 7 and the other using ammonium-saturated bentonite 7; thus equilibrium was approached in both directions. The equilibrated mixtures were filtered, and the filtered solutions

were analyzed for both calcium and ammonium. The final amounts of CaZ_2 and NH_4Z present in the mixtures were calculated as the difference between the total amounts of calcium and ammonium in the system and that found in the solution. The experimental data are presented in tables 8 and 9.

In column 9, tables 8 and 9, are given the values for a dibasic complex anion; the values are the same for both the mixed crystal hypothesis and for Kerr's method of dealing with the solid phases. Column 10 gives the values for the equilibrium constant for a monobasic anion calculated by the use of equation F, Kerr's equation. The last column contains the constant for a monobasic anion calculated by the use of equation G for the mixed crystal hypothesis.

It is evident that equation G gives a very much better representation of these experimental data than does Kerr's equation; thus it seems probable

TABLE 9

Experimental data for bentonite 7 for the reaction $2\,NH_4Z + Ca^{++} = CaZ_2 + 2\,NH_4^+$, *equilibrium approached from the right*

(Concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS		
				By analysis		Calculated		Dibasic anion	Monobasic anion	
NH_4Z	CaZ_2	NH_4^+	Ca^{++}	NH_4^+	Ca^{++}	NH_4Z	CaZ_2		Equation F	Equation G
0.0	20.0	20.0	80.0	17.6	82.4	2.4	17.6	28	11.5	130
0.0	40.0	40.0	60.0	31.8	68.2	8.2	31.8	57	7.0	169
0.0	60.0	60.0	40.0	42.5	57.8	17.5	42.2	75	4.3	166
0.0	80.0	80.0	20.0	51.4	49.7	28.6	50.3	94	3.3	177
0.0	100.0	100.0	0.0	57.6	43.7	42.4	56.3	102	2.4	169
0.0	80.0	100.0	0.0	62.8	39.1	37.2	40.9	112	3.0	173
0.0	60.0	100.0	0.0	67.8	33.1	32.2	26.9	116	3.6	164
0.0	40.0	100.0	0.0	74.7	25.7	25.3	14.3	122	4.8	156
0.0	20.0	100.0	0.0	85.2	15.5	14.8	4.5	142	9.6	163

that for this particular bentonite the partial substitution of one cation for another produces a mixed crystal or solid solution rather than two solid phases behaving either as independent phases or as if in solution.

By taking the logarithms of equations F and G they can be written in the forms

$$\log\left(\frac{Ca^{++}}{NH_4^{+2}}\right) = \log\left(\frac{CaZ_2}{NH_4Z^2}\right) - \log K \qquad (H)$$

and

$$\log\left(\frac{Ca^{++}}{NH_4^{+2}}\right) = \log\left[\frac{CaZ_2(CaZ_2 + NH_4Z)}{NH_4Z^2}\right] - \log K \qquad (I)$$

respectively. Both of these equations are in the form of the straight line equation with a slope of unity. The data in table 9 are plotted as the solid circles in figure 2 according to equations H and I; the quantities $\log\left(\frac{Ca^{++}}{NH_4^{+2}}\right)$ are the ordinates, and the quantities $\log\left(\frac{CaZ_2}{NH_4Z^2}\right)$ and $\log\left[\frac{CaZ_2(CaZ_2+NH_4Z)}{NH_4Z^2}\right]$ are the abscissas. The curve on the left is the one for equation H and the one on the right is for equation I. Figure 2 shows graphically what was brought out in tables 8 and 9, that the mixed crystal hypothesis offers a better explanation of the behavior of this bentonite than does Kerr's equation. Both

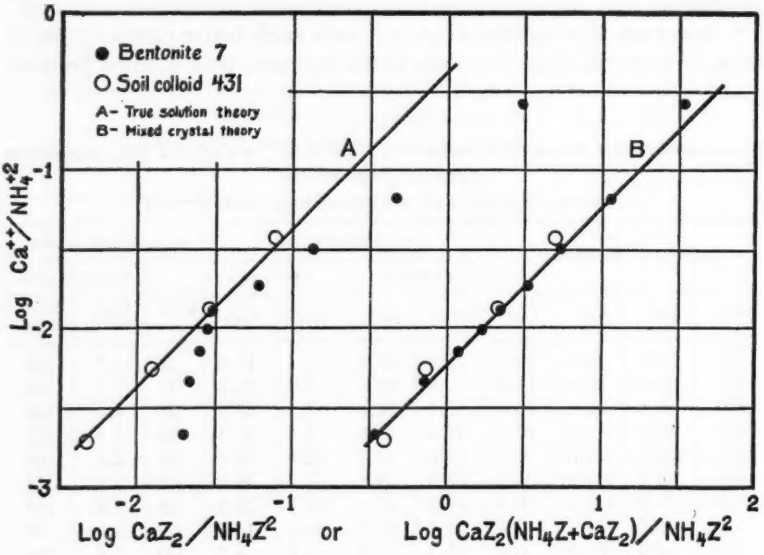

FIG. 2. EQUILIBRIA IN THE CALCIUM-AMMONIUM EXCHANGE REACTIONS OF BENTONITE 7 AND SOIL COLLOID 431

the lines in figure 2 are drawn with the theoretical slope of unity, and the experimental points should fall on or near the line. This they do when plotted according to the mixed crystal equation, but do not when plotted according to Kerr's equation.

The open circles in figure 2 represent a few somewhat similar experiments with soil colloid 431 and are plotted in the same manner as the bentonite data. The experimental data for these experiments with soil colloid 431 are given in table 10.

These experiments with soil colloid 431 were performed at a temperature of 25°C., the solutions were analyzed for both calcium and ammonium; and the quantities CaZ_2 and NH_4Z were calculated by difference. It will be noted that

a constant amount (100 m. e. per liter) of the material was used in these experiments, and for this reason there is little to choose between the two hypotheses; the constants of both equations F and G are fairly uniform, those calculated by Kerr's equation being perhaps a shade more constant. But it is only by varying the amount of bentonite used that the inadequacy of Kerr's formula is brought out. The equation for the equilibrium constant derived on the assumption of mixed crystal formation brings the data for soil colloid 431 into accord with that of bentonite 7. In contrast to this, only one of the bentonite 7 points (the one in which 100 m.e. per liter were used) falls on the line passing through the soil colloid 431 data when plotted according to equation H. The applicability of any theoretically derived formula should not be limited by the necessity of using a constant amount of base-exchange material, as Kerr's equation obviously is.

Kerr (6) studied the calcium-ammonium exchange reaction for an oxidized Hawaiian soil. He used the same amount of soil throughout his series of ex-

TABLE 10

Experimental data for soil colloid 431 for the reaction $2\,NH_4Z + Ca^{++} = CaZ_2 + 2\,NH_4^+$, *equilibrium approached from the right*

(Concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS	
NH_4Z	CaZ_2	NH_4^+	Ca^{++}	NH_4^+	Ca^{++}	NH_4Z	CaZ_2	Equation F	Equation G
0.0	100.0	69.8	30.1	40.2	61.4	29.6	68.7	2.06	132
0.0	100.0	99.8	0.0	57.2	43.6	42.6	56.4	2.29	162
30.0	70.0	99.8	0.0	72.7	29.4	57.1	40.6	2.24	173
60.0	40.0	99.8	0.0	87.3	15.1	72.5	24.9	2.19	183

periments, consequently his data give constant values for the equilibria constants when substituted into his equation. His data, when substituted into the mixed crystal equation, give a value of about 75 for the reaction constant, as compared to a value of about 170 for bentonite 7 and soil colloid 431. This difference is in all probability due to the fact that Kerr used a different soil from those used here; although other factors, such as differences in temperature and concentrations, no doubt also contribute to the difference. The investigation of the sodium-potassium exchange reaction showed that there are at least two types of soils and bentonites from the standpoint of the physical chemistry of the exchange reaction.

HYSTERESIS OF THE EXCHANGE REACTION

The phenomenon of hysteresis, or the failure to attain a true equilibrium, was investigated more fully. By using equivalent amounts (20 m.e. per liter) of calcium-saturated bentonite 7 and ammonium chloride solution, and am-

monium-saturated bentonite 7 with calcium coloride solution, equilibrium for the reaction

$$2\ NH_4Z + Ca^{++} = CaZ_2 + 2\ NH_4^+$$

was approached in both directions. One set of experiments was performed at room temperature with only 5 hours elapsing before the solutions were filtered off for analyses. The other set of experiments was given frequent shaking for 7 days at a temperature of 75°C. The experimental data are presented in table 11. The solutions were analyzed for calcium and ammonium; the quantities CaZ_2 and NH_4Z were calculated by difference and the equilibrium constants by the use of equation G. The ratio of the values for the "equalibria constants," approached in opposite directions is given in the last column. It is evident from the values of this ratio, that the approach to a true equilibrium

TABLE 11

Effect of time and temperature on the attainment of equilibrium in the reaction $2\ NH_4Z + Ca^{++} = CaZ_2 + 2\ NH_4^+$

(Concentrations expressed in milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS	RATIO OF EQUILIBRIUM CONSTANTS
NH_4Z	CaZ_2	NH_4^+	Ca^{++}	NH_4^+	Ca^{++}	NH_4Z	CaZ_2		
5 hours shaking at room temperature									
19.68	0.0	0.0	20.06	12.68	7.47	7.00	12.59	73	0.39
0.0	20.00	20.12	0.0	14.37	5.91	5.75	14.09	190	
7 days shaking at a temperature of 75°C.									
19.68	0.0	0.0	20.06	14.51	5.84	5.17	14.22	237	0.45
0.0	20.00	20.12	0.0	15.90	4.80	4.22	15.20	530	

is not significantly better in the experiments conducted at 75°C. for 7 days than in those at room temperature for only 5 hours. If it were a question of rate of reaction and sufficient time for the attainment of equilibrium, one would expect a much closer approach to a true equilibrium in those experiments conducted at a temperature of 75°C., at which temperature the rate of reaction would probably be 100 or so times greater. Furthermore, a similar set of experiments which were kept at a temperature of 75°C. for 2 days and then cooled and allowed to remain at room temperature for 5 days gave results almost identical with those obtained in the experiments conducted at room temperature (table 11). The values for the reaction constants were 90 and 200, giving a ratio of 0.45. That experiment in which ammonium-saturated bentonite and calcium chloride solution were used had, on being heated to 75°C., reacted to a greater extent than the system calcium-saturated bentonite and ammonium chloride solution does at room temperature; and yet on cool-

ing and standing at room temperature, little if any effect of the higher temperature remained.

This phenomenon of hysteresis is not confined to bentonites, but occurs also in the exchange reactions of soils, permutites, and zeolites, as has already been mentioned. Neither is it true that all exchange reactions of one substance show this hysteresis. There is little indication of hysteresis in the reaction

$$BaZ_2 + Ca^{++} = CaZ_2 + Ba^{++}$$

as the data presented in table 12 show. These experiments were conducted at 40°C. for 2 days. The solutions were analyzed for both barium and calcium; the quantities BaZ_2 and CaZ_2 were calculated by difference. Similarly, the reaction

TABLE 12

Experimental data for bentonite 7 for the reaction $BaZ_2 + Ca^{++} = CaZ_2 + Ba^{++}$

(Concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS	RATIO OF EQUILIBRIUM CONSTANTS
BaZ_2	CaZ_2	Ba^{++}	Ca^{++}	Ba^{++}	Ca^{++}	BaZ_2	CaZ_2		
20.00	0.0	0.0	20.05	9.58	10.50	10.42	9.55	0.837	0.98
0.0	20.00	19.86	0.0	9.54	10.41	10.32	9.59	0.851	

TABLE 13

Experimental data for bentonite 7 for the reaction $BaZ_2 + Cu^{++} = CuZ_2 + Ba^{++}$

(Concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS	RATIO OF EQUILIBRIUM CONSTANTS
BaZ_2	CuZ_2	Ba^{++}	Cu^{++}	Ba^{++}	Cu^{++}	BaZ_2	CuZ_2		
20.00	0.0	0.0	19.98	9.38	10.64	10.62	9.34	0.775	0.98
0.0	20.00	19.87	0.0	9.35	10.61	10.52	9.39	0.787	

$$BaZ_2 + Cu^{++} = CuZ_2 + Ba^{++}$$

shows little if any indication of hysteresis; the experimental data for this reaction are presented in table 13. These experiments were conducted at 40°C. for only 3 hours. The final solutions were analyzed for both copper and barium. The final quantities of BaZ_2 and CuZ_2 were calculated by difference.

Kerr (5) studied the calcium-magnesium exchange reaction; and in the case of the Miami silt loam equilibrium was approached in both directions with no evidence of any hysteresis for this reaction.

Hisschemöller (3) studied the reaction

$$NH_4Z + Na^+ = NaZ + NH_4^+$$

for permutites and found very marked hysteresis. By repeatedly transforming the permutite back and forth from a sodium-saturated to an ammonium-saturated condition at room temperature he found that the hysteresis was removed. The author subjected some bentonite 7 to 5 complete calcium-ammonium transformations and then investigated the calcium-ammonium exchange reaction for this material, but found no closer approach to a true equilibrium.

The calcium-ammonium exchange reaction for soil colloid 431 was investigated in the same manner, the data being given in table 14. These experiments were conducted at room temperature for a period of 24 hours. The final solutions were analyzed for both calcium and ammonium; the final quantities of CaZ_2 and NH_4Z were calculated by difference and the constants by equation G. The results are in fair agreement with the room temperature values of bentonite 7.

This phenomenon of hysteresis may possibly be related to some phase of the crystal structures of the base-exchange substances. The fact that none of the

TABLE 14

Experimental data for soil colloid 431 for the reaction $2\,NH_4Z + Ca^{++} = CaZ_2 + 2\,NH_4^+$

(Concentrations expressed as milligram equivalents per liter)

INITIAL CONCENTRATIONS				FINAL CONCENTRATIONS				EQUILIBRIUM CONSTANTS	RATIO OF EQUILIBRIUM CONSTANTS
NH_4Z	CaZ_2	NH_4^+	Ca^{++}	NH_4^+	Ca^{++}	NH_4Z	CaZ_2		
19.40	0.0	0.0	19.93	12.15	8.09	7.25	11.84	54	0.35
0.0	20.00	19.98	0.0	13.98	6.29	6.00	13.71	153	

exchange reactions involving two divalent cations showed appreciable hysteresis in the case of the bentonite 7 seems of significance to the author, especially when one remembers that this bentonite contains only divalent cations. The author, however, offers no explanation of this phenomenon.

SUMMARY

The author realizes that this work can be considered only as being of a preliminary nature, as too few soil colloids, bentonites, and zeolites have been investigated to draw any sweeping conclusions. But the few results thus far obtained confirm the conclusions of other investigators that the base-exchange constituents of soils and bentonites are remarkably similar, and that permutites and zeolites differ from the base-exchange complex of soils in many respects.

The investigation of the sodium-potassium exchange reactions of bentonites and soil colloids showed that there are at least two and very probably more classes of bentonites and soil colloids. The results further indicate that the base-exchange complex anions of bentonites and soils are monobasic, in harmony with the work of Kerr.

The results of the experimental investigation of the calcium-ammonium exchange reactions of a bentonite and a soil colloid can best be interpreted by the hypothesis of the formation of a mixed crystal when one replaceable cation is partially replaced by another cation.

The sodium-potassium and the calcium-ammonium exchange reactions of all the materials that were studied showed pronounced hysteresis, or failure to attain "true" equilibria. An attempt to remove, by repeated transformation, the hysteresis in the calcium-ammonium exchange reaction of a bentonite failed to reduce it appreciably. On the other hand, in the case of the bentonite, none of the exchange reactions involving two divalent cations showed any appreciable amount of hysteresis. Experimental evidence indicates that it probably is not a question of rate of reaction or insufficient time for the attainment of equilibrium, but is probably a phenomenon associated with the crystal structure of the alumino-silicates.

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DEHYDRATION, SOIL ACIDITY, AND EXCHANGEABLE BASES*

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In a previous communication the authors have discussed the effect of heat and dehydration upon the acidity of suspensions of soil, and have shown that the increased acidity observed is accompanied by a diminution of the content of exchangeable bases, and an increase in the amount of those present in the solution in contact with the soil (3).

The object of the work which is contained in the present paper is to obtain further information upon the extent of these changes, and to trace the effect of these changes upon the associated anion.

EXPERIMENTAL METHODS

The method employed in measuring the pH of the soils was that described by Bülman (2). A list of the soils employed together with their mechanical analyses, which were worked out under the new international method, is given in table 1.

INVESTIGATION OF THE EFFECT OF HEATING UPON THE EXCHANGEABLE AND WATER-SOLUBLE BASES OF SOILS

Previous experiments showed that the total exchangeable bases in soils were less after heating the soil in a steam oven than in the original soil. The total bases in that work were estimated by the acid neutralization method (3).

In the present work the bases were estimated individually. The soils were leached with normal ammonium chloride and also with water. The ammonium chloride extract will contain the exchangeable bases, plus the water-soluble bases, so that the difference between the bases in the ammonium chloride extract and those in the water extract gives the amount of exchangeable bases. The experimental details were as follows:

In every case, 30 gm. of the damp soil and 25 gm. of the soil previously heated for 48 hours in the oven were used. The soil was weighed out into a beaker and 100 cc. of hot normal ammonium chloride solution added and the mixture was left to stand with occasional stirring overnight. At the same time another exactly similar experiment was performed using water instead of ammonium chloride. In all cases the ammonium chloride and water leachings were done side by side. After standing overnight the liquid was decanted through a filter and the soil was washed on to the filter with ammonium chlo-

ride and water respectively. The leaching was then continued until the volumes of the respective filtrates were exactly 1 liter. The bases calcium, magnesium, potassium, sodium, were then estimated in the ammonium chloride and water extracts, and the results expressed as milligram equivalents of base per 100 gm. of dried soil.

In the case of the soil 4, which contains calcium carbonate, a similar leaching with normal sodium chloride, instead of ammonium chloride, was performed for the estimation of the calcium.

TABLE 1

Mechanical analysis of the soils

ORIGIN AND DESCRIPTION OF SOILS	LOSS ON IGNITION	COARSE SAND	FINE SAND	SILT	CLAY	CALCIUM CARBONATE
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1. Downwash from plateau gravel on Kimeridge clay over Coral rag, forest soil	13.27	35.49	12.38	10.85	26.30	....
2. Downwash from plateau gravel on Kimeridge clay over Coral rag, forest soil	13.00	7.32	33.70	20.35	28.42	....
3. Kimeridge clay, pasture soil	10.67	13.67	20.94	22.16	33.42	....
4. Middle lias calcareous ironstone, arable loam	10.59	14.72	26.88	24.00	27.02	0.06
5. Kimeridge clay forest subsoil	4.78	17.33	22.34	19.05	34.81	....
6. Red loam soil from Devon	7.82	24.10	25.23	21.35	22.95	....
7. Fen soil from Peterboro District, Northants	29.93	9.08	11.70	17.33	35.87	....
8. Soil from edge of fens, Cambridge	10.15	0.26	15.42	28.30	47.57	1.19
9. Soil from edge of fen, Cambridge	14.14	0.56	26.94	23.77	36.25	0.35
10. Laterite from Sierra Leone, W. Africa	14.95	29.08	6.98	11.60	48.40	....
11. Ibadakuli soil, Tanganyika, E. Africa	3.93	47.15	23.56	5.60	21.65	....
12. Kondoa-Irangi Dodoma, Tanganyika, E. Africa	5.95	14.76	11.04	16.65	57.75	....
13. Peat from Co. Wicklow, Ireland	.....	.....	.....	.....	.....	....
14. Kimeridge clay, heavy pasture soil	14.25	2.62	6.20	17.54	60.72	....
15. Old red sandstone, clay subsoil, Hereford	2.57	3.53	23.38	47.87	23.00	....
16. Old red sandstone, clay subsoil, Hereford	4.13	1.17	15.06	51.27	32.42	....

The calcium was estimated by precipitation as oxalate and titrating with permanganate the oxalic acid formed by the action of sulfuric acid upon this. The magnesium was estimated by precipitation as phosphate and weighing, the potassium by weighing as perchlorate, and the sodium by weighing as sulfate. The results are given in table 2 and show clearly that the amounts of bases present in the ammonium chloride extracts are the same before and

after heating, but that there are more water-soluble bases after heating than there were before. Consequently there are less exchangeable bases in the soil after the drying, thus confirming the previous work. Further, these results

TABLE 2

Effect of 48 hours' heat on the soils

Results expressed in milligram-equivalents per 100 gm. dry soil

BASE	BEFORE HEATING			AFTER HEATING		
	NH_4Cl extract	Water extract	Exchangeable bases	NH_4Cl extract	Water extract	Exchangeable bases
Soil 1						
Calcium	39.46	1.72	37.74	39.44	3.12	36.32
Magnesium	2.72	0.21	2.51	2.76	0.86	1.90
Potassium	0.81	0.29	0.52	0.81	0.35	0.46
Sodium	1.91	0.48	1.43	1.93	0.65	1.28
Total	44.90	2.70	42.20	44.94	4.98	39.96
Soil 2						
Calcium	34.72	1.17	33.55	34.65	2.74	31.91
Magnesium	2.26	0.08	2.18	2.19	0.18	2.01
Potassium	0.72	0.17	0.55	0.76	0.43	0.33
Sodium	3.14	1.40	1.74	3.20	1.85	1.35
Total	40.84	2.82	38.02	40.80	5.20	35.60
Soil 3						
Calcium	16.40	0.76	15.64	16.31	1.80	14.51
Magnesium	2.42	0.21	2.21	2.78	0.86	1.92
Potassium	0.78	0.14	0.64	0.71	0.25	0.46
Total	19.60	1.11	18.49	19.80	2.91	16.89
Soil 4						
Calcium	22.44	1.78	20.66	22.76	3.48	19.28
Magnesium	1.53	0.32	1.21	1.52	0.54	0.98
Potassium	0.63	0.21	0.42	0.61	0.30	0.31
Sodium	2.11	0.90	1.21	2.12	0.97	1.15
Total	26.71	3.21	23.50	27.01	5.29	21.72

indicate that the heating has the effect of changing some of the exchangeable bases into water-soluble bases.

EFFECT OF ALTERNATE WASHING AND DRYING ON THE pH OF SOILS

It was discovered while experimenting with soil 5 that, although boiling up the dried soil with water and evaporating off the water had no effect on the pH

TABLE 3

Effect of alternate washing and drying on pH of soils

	SOIL 2	SOIL 2A*	SOIL 5	SOIL 6	SOIL 7	SOIL 8	SOIL 9	SOIL 10	SOIL 11	SOIL 12	SOIL 13
pH of original soil	6.88	4.47	4.37	5.19	6.60	6.88	5.78	5.00	5.83	4.94	4.05
pH after 48 hours in oven	6.52	3.89	3.41	4.62	6.27	6.39	5.42	4.31	5.26	4.22	3.58
pH after washing and reheating for 48 hours	6.10	3.47	3.22	4.43	6.10	6.56	5.70	4.15	4.51	4.11	3.57
pH after washing and reheating for 48 hours	5.76	3.64	2.99	4.26	5.99	6.11	5.31	4.21	4.03	3.64	3.56
pH after washing and reheating for 48 hours	5.27	3.24	2.99	4.11	5.87	6.35	5.44	3.99	3.62	3.25	....
pH after washing and reheating for 48 hours	5.06	3.00	2.99	4.05	5.67	5.69	5.40	3.63	3.86	3.11	....
pH after washing and reheating for 48 hours	4.85	3.39	....	3.99	5.58	6.07	5.08	3.68	3.70	3.10	....
pH after washing and reheating for 48 hours	4.51	3.00	....	3.92	5.35	5.66	4.89	3.42	2.89	2.77	....
pH after washing and reheating for 48 hours	4.27	3.69	....	3.84	4.56	5.53	4.98	3.28	2.80	2.54	....
pH after washing and reheating for 48 hours	4.04	3.64	....	3.64	5.05	5.80	4.96	3.18	2.73	2.65	....
pH after washing and reheating for 48 hours	3.95	2.98	....	3.62	5.06	5.50	4.88	3.40	2.97	2.81	....
pH after washing and reheating for 48 hours	3.80	3.34	....	3.54	4.16	5.71	4.33	3.25	3.09	2.45	....
pH after washing and reheating for 48 hours	3.68	3.05	....	3.42	4.89	5.12	4.46	3.28	3.39	2.51	....
pH after washing and reheating for 48 hours	3.40	....	....	3.38	4.85	....	4.00	3.20	2.95	2.36	....
pH after washing and reheating for 48 hours	3.40	....	....	3.32	4.75	4.24	3.94	3.22	2.90	2.37	....
pH after washing and reheating for 48 hours	3.40	....	....	3.22	4.64	3.65	3.84	3.20	3.20	2.76	....
pH after washing and reheating for 48 hours	3.41	....	....	3.10	4.48	3.99	3.75	3.13	3.02	2.35	....
pH after washing and reheating for 48 hours	....	....	....	3.03	4.39	3.10	3.61	3.13	2.88	2.76	....
pH after washing and reheating for 48 hours	....	....	....	2.92	4.31	3.27	3.43	3.01	2.84	2.36	....
pH after washing and reheating for 48 hours	....	....	....	2.92	4.28	3.05	3.20	3.01	....	2.26	....
pH after washing and reheating for 48 hours	....	....	....	....	4.14	3.08	3.36	....	....	2.16	....
pH after washing and reheating for 48 hours	....	....	....	....	3.96	2.61	3.29	....	....	2.23	....
pH after washing and reheating for 48 hours	....	....	....	....	3.78	2.40	3.12	....	....	....	....
pH after washing and reheating for 48 hours	....	....	....	....	3.72	2.50	3.10	....	....	....	....

TABLE 3—*Concluded*

	SOIL 2	SOIL 2A*	SOIL 5	SOIL 6	SOIL 7	SOIL 8	SOIL 9	SOIL 10	SOIL 11	SOIL 12	SOIL 13
pH after washing and reheating for 48 hours	....	....	....	....	3.59	2.62	3.15	....	....	....	....
pH after washing and reheating for 48 hours	....	....	....	....	3.36	....	2.95	....	....	....	....
pH after washing and reheating for 48 hours	....	....	....	....	3.38	....	3.11	....	....	....	....
pH after washing and reheating for 48 hours	....	....	....	....	3.26	....	2.72	....	....	....	....
pH after washing and reheating for 48 hours	....	....	....	....	3.04	....	....	....	....	....	....
pH of heated base-free soils	2.84	....	2.99	3.00	2.83	2.58	2.58	2.81	2.50	1.81	2.56

* Soil 2, after treatment with hydrogen peroxide.

of the soil, leaching the dried soil with distilled water and again heating, caused the pH to fall. On repeating the procedure several times the pH became constant at a figure closely approximating the pH of the base-free soil prepared by leaching with dilute hydrochloric acid, and in addition the soil was found to contain no exchangeable bases.

Further experiment on soil 2 demonstrated the fact that merely leaching the heated soil with water caused the pH to rise slightly as a result of partial recovery of the soil, but that on heating this leached soil for 48 hours the pH fell again to a figure below that of the soil before the leaching was commenced.

Again, the effect of boiling up the soil with water before leaching was investigated, and this showed that such treatment did not produce a bigger decrease in pH than the leaching with cold water alone. As a result of these experiments it was decided to investigate the effect of alternate leaching and drying on a number of different soils.

About 200 gm. of the soil was used at the start of each experiment, and each soil was first heated for 48 hours in the steam oven at approximately 98°C. The pH was measured and then the soil was leached with about 2,000 cc. of water. The washing was done by decantation in a beaker, all the liquid being run through a filter so as to avoid any loss of fine material. At the conclusion of the leaching the soil was washed off the paper and beaker with hot water into an evaporating dish, and the liquid was evaporated off on the water bath. The soil was then passed through a 1-mm. sieve and heated for 48 hours in the oven again. The whole process was then repeated a number of times and the results are given in table 3. In the case of soil 7 the experiment had to be stopped before the end of the reaction because all the soil had been used up.

The results showed that in all cases except soils 2, 12, and 13, the pH tended to become constant at a value approximating that of the base-free soil prepared by leaching with dilute hydrochloric acid.

It is interesting to note that the reaction of the peat soil 13, although becoming more acid after the original heating in the oven, remained constant following the subsequent washing and drying operations. This indicates that the changes occurring in the other soils are a function of the inorganic constituents of the soils.

TABLE 4

Effect of alternate washing and drying on the water-soluble constituents of soil

Results in mgm. per 100 gm. dry soil

*Soil 6**

	CALCIUM	ALUMINUM	SULFATE
A	40.46	1.88	103.60
B	28.55	0.88	70.56
C	20.22	2.17	60.65
D	17.30	3.38	55.70
E	15.06	2.26	38.98
F	11.98	3.60	42.70
G	6.29	2.54	37.13
H	5.24	3.32	30.94
I	8.24	3.61	37.13
J	5.99	3.39	47.02
K	5.99	3.60	63.10
L	2.99	4.03	69.95
M	2.55	3.60	30.94
N	1.50	3.39	37.13
O	1.05	3.39	34.03
P	1.50	3.80	41.46
Q	3.75	4.23	54.45
R	2.25	3.68	55.70
S	1.20	4.45	32.19
T	4.49	3.84	33.42
U	3.75	3.68	44.55
V	4.49	3.93	34.03
W	3.75	3.60	35.28
X	1.50	3.45	25.99
Y	1.50	3.84	23.52
Z	1.05	3.60	21.05
a	0.72	3.76	43.93
b	0.72	3.53	37.13
c	0.00	3.38	29.70
d	0.00	3.45	33.42
e	0.00	4.51	41.51
f	0.00	4.51	26.18
Total.....	204.08	110.28	1,373.07
Exchangeable calcium left in soil.....	0.00	.....	.....
Total exchangeable calcium.....	202.30	.....	.....

TABLE 4—*Continued*

Soil 14†

	CALCIUM	IRON	ALUMINUM	SULFATE	PHOSPHATE
A	80.40	0.5	2.25	394.4	Trace
B	57.00	1.22	2.0	340.0	5.04
C	52.60	2.92	2.25	252.0	5.60
D	46.00	2.05	3.0	236.0	5.80
E	42.40	4.43	3.0	148.0	5.71
F	34.40	4.56	3.0	228.0	5.09
G	28.60	3.76	3.0	132.0	4.08
H	24.00	7.49	4.0	148.0	3.90
I	38.00	8.77	7.0	148.0	3.09
J	20.00	11.30	9.0	152.8	2.50
K	16.0	11.43	10.0	194.4	2.00
L	18.0	11.43	10.0	84.0	1.60
M	20.93	8.25	10.0	110.4	1.16
N	11.6	11.80	12.0	132.0	1.26
O	12.4	9.00	8.0	95.2	0.72
P	4.4	7.00	8.0	60.0	0.32
Q	2.67	8.75	8.0	68.0	0.64
R	2.8	8.12	7.0	76.0	0.47
S	3.73	8.32	8.0	64.0	0.40
T	2.67	2.88	3.2	30.4	0.59
U	2.4	4.00	4.0	32.0	1.12
V	2.4	3.75	4.0	27.4	1.12
W	2.0	3.62	3.5	25.6	0.93
X	2.4	5.00	4.0	36.0	0.55
Y	2.27	3.50	3.0	21.6	0.48
Z	2.0	3.65	2.1	21.6	0.79
a	2.4	3.44	3.0	30.4	0.50
b	1.6	4.00	3.0	22.66	0.70
c	1.33	2.78	3.0	17.2	0.30
d	2.0	3.50	3.0	25.2	0.46
e	0.8	2.00	3.0	44.0	0.51
f	0.8	1.11	2.0	33.2	0.31
g	1.04	1.58	3.0	22.8	0.45
h	0.8	2.37	1.0	6.8	0.16
i	0.8	1.33	1.0	16.0	0.13
j	0.8	1.77	2.0	26.0	0.39
k	1.2	1.69	1.0	10.0	0.17
l	1.04	1.55	1.0	14.8	0.14
m	0.8	1.82	1.0	6.0	0.20
n	0.8	1.45	2.0	18.0	0.08
o	0.8	1.06	1.0	10.0	0.04
p	0.8	1.80	1.0	15.2	0.00
q	0.64	1.04	1.0	16.0	0.04
r	0.64	0.44	1.0	10.0	0.05
s	0.00	0.80	1.0	8.0	0.05
t	0.00	0.66	1.0	7.2	0.05
u	0.00	0.99	0.5	6.8	0.10
Total.....	551.16	194.68	178.8	3,624.06	59.79
Exchangeable calcium remaining in soil.....	0.00	.....	.....	.....	.....
Total exchangeable calcium.....	560.00	.....	.....	.....	.....

TABLE 4—*Concluded*

Soil 15‡

	CALCIUM	IRON	ALUMINUM	SULFATE	CHLORIDE
A	12.12	0.86	3.33	21.41	4.23
B	4.0	0.8	1.0	13.2	3.50
C	3.2	0.37	0.25	11.2	Nil
D	6.67	1.0	2.0	31.2	Nil
E	4.0	1.33	2.0	23.2	
F	4.0	1.5	1.0	23.2	
G	1.33	0.99	1.0	16.4	
H	2.96	0.67	1.0	10.0	
I	1.2	0.90	1.0	9.2	
J	0.8	1.66	0.5	5.2	
K	0.56	0.58	1.0	11.2	
L	2.0	0.8	0.25	5.2	
M	0.8	0.62	1.0	9.2	
N	0.0	0.8	0.5	4.2	
O	0.8	1.03	1.0	6.0	
P	0.8	1.12	1.0	6.8	
Q	1.2	0.32	1.0	10.8	
R	0.0	0.33	0.5	4.0	
S	0.0	0.28	0.45	2.8	
T	0.0	0.30	0.4	3.2	
Total.....	46.44	16.26	20.18	227.61	7.73
Exchangeable calcium left in soil.....	182.60	.....	.....	.....	....
Total exchangeable calcium.....	236.80	.....	.....	.....	....

Soil 16§

	CALCIUM	IRON	ALUMINUM	SULFATE	PHOSPHATE	CHLORIDE
A	2.93	0.92	3.0	30.0	Trace	0.70
B	2.67	0.70	3.0	26.0	Nil	Nil
C	2.00	0.70	3.0	27.2	Nil	Nil
D	1.33	0.88	1.0	24.0	Trace	
E	1.33	1.50	1.0	14.0	Nil	
F	1.20	0.77	1.0	11.2	Nil	
G	1.20	0.64	1.0	6.8	Nil	
H	1.20	0.71	1.0	8.0		
I	0.56	1.06	1.0	9.2		
J	0.00	0.58	1.0	7.6		
K	0.00	0.71	0.5	5.2		
L	0.00	0.75	1.0	7.6		
Total.....	14.42	9.92	17.5	176.8	.....	0.7
Exchangeable calcium left in soil.....	0.00	....	....	.....	.....	....
Total exchangeable calcium...	12.60	....	....	.....	.....	....

* Soil 6 A nitrite present, chloride nil; 6 B nitrite faint trace, chloride nil; 6 C nitrite very faint trace, chloride nil; 6 D chloride nil.

† Soil 14 A nitrate trace; chloride nil; 14 B nitrate and chloride nil; 14 C nitrate nil.

‡ Soils 15 A and B phosphate and nitrate nil, 15 C phosphate nil.

§ Soils 16 A and B nitrate nil.

The object of the next set of experiments was to discover the anions in combination with which the bases came into the water solution during the process of alternate heating and washing the soils. Preliminary qualitative experiments showed that considerable quantities of sulfates were present in the aqueous extracts. As a result of this it was decided to make quantitative estimations of sulfates in the solution and also of other anions such as chloride, nitrate, phosphate. The following procedure was adopted: Twenty-five grams of soil which had been heated for 48 hours at 98°C. in the water oven were taken. The soil was placed in a beaker with 100 cc. of distilled water and left overnight with occasional stirring. The liquid was then decanted through a hard filter paper into a liter flask, after which the soil was all washed on to the filter. The soil was then leached with distilled water until the filtrate was exactly 1 liter. Estimations of the calcium, sulfate, etc., in this solution were made and the results are given as A in table 4. The soil was then heated for 48 hours in the oven without removing it from the filter paper, after which a liter of water was leached through it. The results of the analysis of this extract are given as B in table 4. The procedure was then repeated a number of times until all the calcium had been removed, the results being given as C, D, E, F, etc., in table 4.

The calcium was determined by precipitation as oxalate and titration with potassium permanganate, the iron by a colorimetric method with ammonium thiocyanate, the aluminum by the colorimetric method of F. W. Atack with alizarin S (1), and the phosphate by the colorimetric method of F. W. Parker and J. F. Fudge (5).

The sulfate was determined by weighing as barium sulfate in the case of soil 6, and in the other soils by the colorimetric method of Gedroiz (4). In addition the amount of exchangeable calcium was determined in the original soil and also the amount of exchangeable calcium remaining after the leaching and drying operations.

The results show that with the exception of soil 15 the total calcium in the water extracts is equal to the amount of exchangeable calcium originally present in the soil, and that, soil 15 again excepted, the soils at the end of the treatment contain no exchangeable calcium. This indicates that in certain soils it is possible to remove all the exchangeable calcium, and doubtless all the other exchangeable bases, by this process of alternate heating and leaching. Further, the results indicate that the exchangeable bases come into solution almost entirely as sulfates.

It seems in addition that the iron and aluminum also come into solution as sulfates. In the case of soils 6 and 14 a large quantity of sulfate was available to come into solution and in both these soils all the exchangeable calcium was removed by the washing and drying operations. In the case of soils 15 and 16 comparatively little sulfate could come into solution. Soil 16 contained very little exchangeable calcium and there was enough sulfate available to cause the removal of all this calcium. Soil 15, however, contained considerably more

exchangeable calcium and there was not enough sulfate coming into solution to bring out all of it, hence the removal of calcium was incomplete.

It is noteworthy that the iron and aluminum sulfates continue to come into solution after all the exchangeable calcium has been removed. A qualitative test proved that the soils still contained sulfates even after the prolonged leaching and drying operations. Possibly the sulfate is absorbed in the soil complex as sulfates of iron and aluminum, and the drying of the soil releases some of these salts which react with the exchangeable bases of the soil.

The experimental work has demonstrated the following facts:

1. The amounts of bases extractable by ammonium (or sodium) chloride are the same before and after heating the soil.
2. There is an increase in water-soluble bases after heating the soil.
3. Alternate washing and heating the soils cause the pH to fall to a figure approximating that of the base-free soils, except in the case of the peat and the soil from Dodoma, Tanganyika.
4. It is possible in some soils to remove all the exchangeable bases by a process of alternate washing and drying at 98°C.
5. The bases go into solution largely as sulfates.
6. The iron and aluminum also go into solution as sulfates and continue to come into solution after all the calcium has been removed.
7. The amount of bases removed from the soil in the water extract after heating depends on the quantity of SO_4'' which can come into solution.
8. The soils still contain sulfates at the end of the washing and heating operations.

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STUDIES ON THE BLUE COLORIMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS[1]

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A review of the various blue colorimetric methods proposed for the determination of phosphorus indicated that no one method[2] had been critically tested with reference to the possible effect of such concentrations of salts as are found in many soils and irrigation waters of semiarid regions. In a study of this question certain additional information was obtained. It is the purpose of this paper to present briefly the results of this work.

EXPERIMENTAL

The method employed in this investigation is that outlined by Truog and Meyer (2). As ordinarily used, 4 cc. of a reagent containing 2.5 per cent ammonium molybdate in 10 *N* sulfuric acid is added to the solution to be tested, the volume increased to 99.5 cc., and then while the volume is being shaken, 6 drops of a 2.5 per cent solution of a stannous chloride added. The blue color developed if phosphate or arsenate be present is then compared with similarly prepared standards. Under certain conditions it is desirable to keep the ammonium molybdate and acid as separate reagents, but in any case the final proportions used should be as indicated in the foregoing.

Effect of varying amounts of stannous chloride

In connection with the use of permanent standards (1), attention has been directed to the fact that stannous chloride solutions supposedly protected from the air by mineral oil will, nevertheless, gradually oxidize. This oxidation is caused by the diffusion of the oxygen of the air through the oil layer. To obtain quantitative information on the effect of small and large variations of stannous chloride, a series of solutions containing the same quantities of PO_4 was prepared, different amounts of this reagent were added to each solution, and at frequent intervals during the period of one hour, comparisons of the

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[2] Toward the close of this investigation a method was published by Zinzadze (4) in which the necessity for using a reducing agent is eliminated. He has reported the effect of varying quantities and kinds of salts on the determination.

color intensity developed were made with permanent glass color standards.[3] To compensate for the gradual appearance of a greenish brown tint, which is caused by the action of stannous chloride upon the ammonium molybdate itself, solutions containing all the reagents minus phosphate were prepared and placed in the control compartment of the Hellige Comparator. Thus the readings represent only that color produced by the ammonium phosphomolybdate itself. The data obtained are recorded in table 1. The relation between the amount of stannous chloride added and the maximum color attained is shown more clearly in figure 1. Up to 0.60 mgm. $SnCl_2 \cdot 2H_2O$ the color is proportional to the amount of reducing agent added. Larger quantities create definite but relatively small increases in color. The addition of 7.38 mgm. $SnCl_2 \cdot 2H_2O$ corresponds to the quantity used by Truog and Meyer (2). It is evident that fairly large deviations from this amount will effect but minor variations in color.

TABLE 1

Effect of varying amounts of $SnCl_2 \cdot 2H_2O$ on total color produced from a given PO_4 concentration

MILLIGRAM OF $SnCl_2 \cdot 2H_2O$ ADDED	READING OF COLOR DISC AT SUCCEEDING INTERVALS FOLLOWING $SnCl_2 \cdot 2H_2O$ ADDITION																
	Minutes																
	1	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	35.0	40.0	45.0	60.0
0.24	0.7	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.2
0.37	1.7	1.7	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.3	1.4	1.3	1.3	1.3	1.3	1.3	1.3
0.48	2.5	2.7	2.7	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
0.60	3.2	3.3	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
0.72	3.5	3.5	3.5	3.4	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
1.23	3.7	3.8	3.8	3.8	3.4	3.3	3.3	3.4	3.3	3.3	3.4	3.4	3.4	3.4	3.4	3.4	3.4
2.46	3.8	3.8	3.8	3.8	3.8	3.5	3.4	3.3	3.3	3.3	3.3	3.3	3.3	3.4	3.3	3.4	3.4
3.69	3.9	4.0	4.2	4.2	4.2	3.9	3.7	3.4	3.3	3.3	....	3.4	3.3	...	...	...	...
7.38*	4.0	4.2	4.2	4.3	4.2	4.1	4.1	4.1	3.7	3.3	3.3	3.3	3.4	3.2	3.3	3.3	3.3
12.3	3.8	4.2	4.3	4.4	4.4	4.4	4.3	4.3	4.3	4.3	4.3	4.0	3.8	3.7	3.7	3.4	3.4
14.7	3.8	4.2	4.3	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.4	4.4	4.0	3.7	3.4	3.2	3.2

* Corresponds to amount of $SnCl_2 \cdot 2H_2O$ used in Truog and Meyer method.

In addition to the foregoing information these data permit some speculation regarding the chemistry involved in this reaction. It will be noted that amounts in excess of 0.60 mgm. $SnCl_2 \cdot 2H_2O$ give a maximum color corresponding to a reading of more than 3.2; however, upon standing, the color fades back to this same level and then remains apparently constant for a long period. This suggests that two or more blue colored compounds are formed, one easily reduced and relatively stable, the other more difficulty reduced and stable only in the presence of excess reducing agent. Wu (3) has presented evidence which

[3] These color standards, ten in number, are mounted on a circular frame especially designed for use in the Hellige Comparator. Each standard is designated by an Arabic numeral and varies sufficiently in color intensity from those adjacent to permit interpolated readings.

indicates that phospho-molybdate complexes can be reduced to different oxidation products. The aforementioned interpretation is thus in harmony with his data.

Effect of SiO_2

According to Truog and Meyer (2), SiO_2 may be present in the final solution in concentrations up to 700.0 p.p.m. without interfering with the usual phospho-molybdate color. It has been found, however, that this noninterference depends upon the manner in which the acid and molybdate reagent are combined with the solution being tested. In solutions of low acidity SiO_2 will unite with molybdate to form a yellow silico-molybdate. This compound will then persist even after the acidity is increased to that concentration requisite for the phospho-molybdate reduction. Upon the addition of stannous chloride this silico-molybdate compound will be reduced to a blue color. After a careful

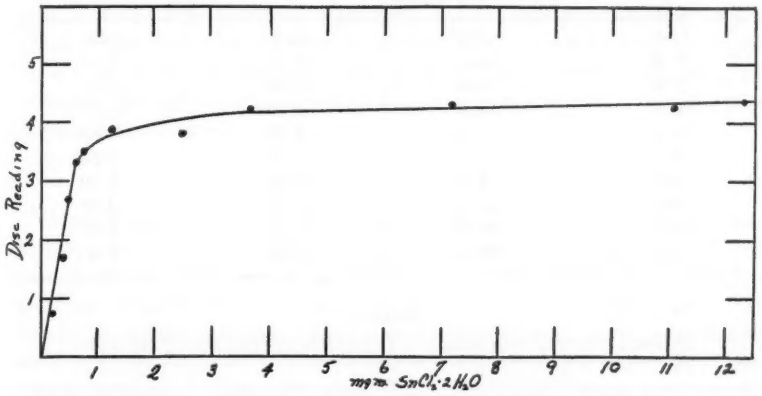

FIG. 1. EFFECT OF VARYING AMOUNTS OF $SnCl_2 \cdot 2H_2O$ ON TOTAL COLOR PRODUCED

study of various methods of combining reagents it was found that conditions are most favorable for the formation of the aforementioned compound when the molybdate reagent is mixed first with the unknown followed then by the slow drop by drop addition of acid. Under these circumstances as little as 0.5 p.p.m. SiO_2 may produce a blue color. On the other hand, if the acid is first added and then the molybdate drop by drop, as much as 700 p.p.m. SiO_2 may be present without interfering.

If the molybdate and acid are united as one reagent the chances of interference by SiO_2 are greatly diminished but still not entirely eliminated. For example, if the first cubic centimeter of acid-molybdate reagent is added drop by drop to a slightly alkaline or neutral solution containing SiO_2, some silico-molybdate will be formed. If, however, this procedure is reversed by adding the solution *to* the acid-molybdate reagent, conditions of acidity are such as to prevent the formation of this compound.

With phosphate or arsenate the manner of combining the acid and molybdate with the solution has no apparent influence upon the formation of their respective molybdates. The determination of SiO_2 in the presence of phosphate or arsenate is thus made possible.

Influence of iron

The author has confirmed the results of Truog and Meyer (2) in which they found that *ferric* iron, in amounts exceeding 4–6 p.p.m. interferes with the determination. This effect can be eliminated by reducing the ferric iron.

TABLE 2

Effect of ferrous iron upon phosphorus determination

CONCENTRATION OF FERROUS IRON IN FINAL SOLUTION	INTERVAL BETWEEN MAKING TO FINAL VOLUME AND ADDITION OF $SnCl_2 \cdot 2H_2O$	CONCENTRATION PO_4 IN STANDARD	CONCENTRATION PO_4 FOUND
p.p.m.	*minutes*	*p.p.m.*	*p.p.m.*
10.0	None	0.76	0.74
10.0	None	0.76	0.75
10.0	None	0.76	0.75
10.0	1.0	0.76	0.66
10.0	3.0	0.76	0.54
10.0	5.0	0.76	0.50
10.0	15.0	0.76	0.48
10.0	90.0	0.76	0.47
10.0	960.0	0.76	0.48

TABLE 3

Influence of varying concentrations of ferrous iron on diminution of blue color

CONCENTRATION OF FERROUS IRON IN FINAL SOLUTION	INTERVAL BETWEEN MAKING TO FINAL VOLUME AND ADDITION OF $SnCl_2 \cdot 2H_2O$	CONCENTRATION PO_4 IN STANDARD	CONCENTRATION PO_4 FOUND
p.p.m.	*minutes*	*p.p.m.*	*p.p.m*
None	5.0	0.76	0.75
1.0	5.0	0.76	0.62
10.0	5.0	0.76	0.50
50.0	5.0	0.76	0.42

However, it has been found that under certain conditions *ferrous* iron may also affect the results. If the test solution containing phosphate and ferrous iron is allowed to stand after being brought to final volume (99.5 cc.) *before* the addition of stannous chloride, the iron will diminish the color that would otherwise have been produced.

To determine how long a solution may thus stand before this effect begins, the following experiment was made: Solutions containing phosphate and 10 p.p.m. Fe as ferrous ammonium sulfate were brought to a volume of 99.5 cc. and allowed to stand for 1, 3, 5, 15, 90, and 960 minutes respectively before the

reducing agent was added. The color developed was then compared with similarly prepared solutions containing no iron, as shown in table 2. The results indicate that ferrous iron in this concentration exerts an effect if the solution standards only 1 minute, and has its maximum effect in about 5 minutes.

The effect of varying quantities of ferrous iron are shown in table 3. Solutions were prepared containing equal amounts of PO_4 but different amounts of ferrous ammonium sulfate. After being made to volume, they were allowed to stand 5 minutes, the stannous chloride was added, and the color was compared with that of iron-free solutions. It was found that under these conditions as little as 1 p.p.m. of ferrous iron will introduce an error. However, if the stannous chloride is immediately added, as high as 750 p.p.m. ferrous iron produced no effect. Under conditions of acidity higher than that of the final solution (0.4 *N*), ferrous iron apparently does not interfere. Hence it is better practice to add the unknown *to* the acid or acid-molybdate reagents. By so doing the acidity of the solution during the process of mixing is always higher than that of the final solution. By following this procedure and adding the stannous chloride as soon as final volume has been attained, no trouble from ferrous iron will be enountered.

Effect of nitrates, chlorides, and sulfates

In studying the influence of nitrates, chlorides, and sulfates upon the determination of phosphate, attention was given both to the immediate and the continued effects. The immediate influence of these salts was determined in solutions of constant PO_4 content but variable amounts of these salts. The color comparisons between standard and unknown were made 2–3 minutes after the addition of the stannous chloride. The continued effect was studied by making comparisons with permanent standards after the lapse of varying periods. The results are given in tables 4 to 9.

Table 4 shows the immediate effect of different nitrates. Above 140 p.p.m. of N, HNO_3 brings about a gradual diminution of the blue phosphate. On the other hand, KNO_3, $NaNO_3$, and NH_4NO_3, in amounts as high as 1,400.0 p.p.m. N, have no immediate influence on the test. Greater amounts slightly intensify the blue color, but even with as much as 12,040 p.p.m. N present in the form of these nitrates, there is less than a 10 per cent increase in the color intensity. In contrast to the effect of these compounds calcium nitrate produces no important effect other than that $CaSO_4$ may be precipitated. This, of course, makes precise readings difficult.

The influence of varying concentrations of $NaNO_3$ on the reaction (table 5), when observed over a period of 1 hour, demonstrates the effect of nitrates upon the fading reaction. With solutions containing no nitrate, the color intensity reaches a maximum corresponding to a reading on the color disc of 4.0. It

TABLE 4

Immediate effect of nitric acid and nitrates upon phosphorus determination

COMPOUND USED	CONCENTRATION OF PO_4 FOUND IN SOLUTIONS WITH VARYING NO_3 CONCENTRATION							
	P.p.m. N as NO_3 in final solution							
	None	1.4	14.0	140.0	700.0	1,400.0	7,000.0	12,040.0
HNO_3	0.75	....	....	0.73	0.69	0.62	....	....
KNO_3	0.75	0.74	0.75	0.74	0.74	0.78	0.83	0.82
$NaNO_3$	0.75	....	0.75	0.75	0.77	0.76	....	0.80
$Ca(NO_3)_2$	0.74	0.78	0.76	0.76	....	0.76	0.73	0.76*
NH_4NO_3	0.75	0.76	0.75	0.78	0.77	0.77	0.82	0.82

*A precipitate of $CaSO_4$ came down at this concentration; hence value is only approximate.

TABLE 5

Effect of $NaNO_3$ on reaction over a period of 60 minutes

CONCENTRATION OF N AS $NaNO_3$ IN FINAL SOLUTION	READING OF COLOR DISC AT SUCCEEDING INTERVALS FOLLOWING $SnCl_2 \cdot 2H_2O$ ADDITION															
	Minutes															
	1	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	35.0	40.0	45.0	60.0
p.p.m.																	
None	3.7	3.9	3.9	3.9	4.0	4.0	4.0	4.0	4.0	4.0	3.7	3.4	3.2	3.2	3.2	3.2	3.2
1.4	3.5	3.8	3.9	3.9	3.9	3.9	3.9	3.9	3.6	3.4	3.3	3.2	3.2	3.0	3.0	3.0	3.0
14.0	3.5	3.7	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.6	3.3	3.1	3.0	3.0	3.0	3.0	3.0
140.0	3.7	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.8	3.3	3.2	3.0	2.9	2.9	2.9	2.9	2.9
700.0	3.5	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.8	3.5	2.8	2.1	1.9	1.2	0.8	0.5	0.2
1,400.0	3.7	4.0	4.0	4.0	4.0	4.0	4.0	3.7	2.8	2.2	1.7	1.4	1.0	0.5	*	*	*
7,000.0	3.7	4.0	4.0	4.0	4.0	4.0	2.8	2.7	1.9	...	1.0	0.7	0.5	0.1	*	*	†
12,040.0	3.9	3.9	4.0	4.0	4.0	3.9	3.7	1.9	0.9	0.7	0.5	...	...	...	†	...	...

* Slight color.

† All gone.

TABLE 6

Effect of sulfates upon phosphorus determination

SALT USED	CONCENTRATION OF PO_4 FOUND IN SOLUTIONS WITH VARYING SO_4 CONCENTRATION							
	P.p.m. SO_4 in final solution							
	None	4.8	48.0	480.0	2,400,0	4,803.0	24,015.0	41,300.0
K_2SO_4	0.76	0.76	0.75	0.73	0.78	0.79	0.87	0.87
$(NH_4)_2SO_4$	0.76	0.78	0.78	0.77	0.82	0.88	0.92	0.87
$MgSO_4$	0.78	0.78	0.79	0.76	0.78	0.81	0.83	0.86

remains apparently constant at this value for about 22 minutes, after which it fades to a color level corresponding to a disc reading of 3.2. In solutions

containing 140 p.p.m. N or more, fading begins sooner and proceeds to a greater degree than in nitrate-free solutions, both of these effects being more pronounced with higher nitrate concentrations. However, under the condi-

TABLE 7

Effect of K_2SO_4 on reaction over period of 60 minutes

CONCENTRATION OF SO_4 IN FINAL SOLUTION	READING OF COLOR DISC AT SUCCEEDING INTERVALS FOLLOWING $SnCl_2 \cdot 2H_2O$ ADDITION																
	Minutes																
	1	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	35.0	40.0	45.0	60.0
p.p.m.																	
None	3.7	3.9	3.9	3.9	4.0	4.0	4.0	4.0	4.0	4.0	3.7	3.4	3.2	3.2	3.2	3.2	3.2
480.3	3.8	3.9	4.0	4.0	4.1	4.1	3.7	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.1
4,803.0	4.1	4.2	4.4	4.4	4.3	4.4	4.4	4.1	3.6	3.6	3.6	3.4	3.4	3.3	3.3	3.2	3.2
24,015.0	4.7	5.0	5.1	5.2	5.3	5.3	4.8	4.5	4.5	4.4	4.3	4.3	4.2	4.2	4.2	4.1	4.0
41,300.0	4.8	5.0	5.2	5.3	5.4	5.4	5.4	5.4	5.4	4.3	4.3	4.3	4.2	4.2	4.1	4.0	3.9

TABLE 8

Effect of chlorides upon phosphorus determination

COMPOUND USED	CONCENTRATION OF PO_4 FOUND IN SOLUTIONS WITH VARYING Cl CONCENTRATIONS							
	P.p.m. Cl in final solution							
	None	3.5	35.4	354.6	1,773.0	3,546.0	17,730.0	30,500.0
HCl	0.76	....	0.77	0.76	0.65	0.58	....	....
NaCl	0.76	0.79	0.78	0.75	0.73	0.71	0.59	0.53
KCl	0.76	0.79	0.79	0.77	0.78	0.72	0.58	0.52
NH_4Cl	0.76	0.79	0.77	0.77	0.73	0.71	0.59	0.52

TABLE 9

Effect of NH_4Cl on reaction over period of 60 minutes

CONCENTRATION OF Cl IN FINAL SOLUTION	READING OF COLOR DISC AT SUCCEEDING INTERVALS FOLLOWING $SnCl_2 \cdot 2H_2O$ ADDITION																
	Minutes																
	1	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	35.0	40.0	45.0	60.0
None	3.7	3.9	3.9	3.9	4.0	4.0	4.0	4.0	4.0	4.0	3.7	3.4	3.2	3.2	3.2	3.2	3.2
354.6	3.7	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.5	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
3,546.0	3.5	3.7	3.8	3.8	3.7	3.7	3.5	3.0	2.9	2.8	2.8	2.7	2.7	2.7	2.7	2.7	2.7
7,730.0	2.9	2.9	2.9	2.9	2.7*	2.5*	2.5*	2.4*	2.3*	2.2*	2.2*	2.2*	2.2*	2.2*	2.2*	2.2*	2.0*
3,500.0	2.4	2.6	2.6	2.0*	2.0*	2.0*	1.8*	1.8*	1.8*	1.5*	1.5*	1.5*	1.5*	1.5*	1.5*	1.5*	1.5*

* Color tint in solution caused by high chlorides makes close readings difficult.

tions of this method and at a temperature of 24°C. no measurable influence upon the reaction was detected within the first 10 minutes even when very high concentrations of the nitrate were present.

Table 6 shows the immediate effect of various sulfates. Solutions containing 2,400 p.p.m. SO_4 or more, somewhat intensify the phosphate color, but the effect is not proportional to the amount of sulfate. Solutions containing 41,300 p.p.m. SO_4, intensified the color less than 15 per cent. There appears to be no difference in the behavior of K_2SO_4, $(NH_4)_2SO_4$, and $MgSO_4$.

The influence of varying amounts of K_2SO_4 on the reaction over a period over a period of 1 hour is shown in table 7. Except for the increase in color which high sulfate produces, there appears to be no other important effect.

The immediate effect of varying concentrations of HCl, NaCl, KCl, and NH_4Cl is shown in table 8. Unlike nitrates and sulfates, high concentrations of chlorides diminish the color. With concentrations of 3,546.0 p.p.m. Cl in the final solution these salts decrease the color about 5 per cent. Corresponding, though not proportional, decreases occur with higher concentrations. The action of free HCl is probably due in part to its effect on the H-ion concentration and is similar to that of other chlorides except that the effect occurs with smaller quantities of the acid.

The effect of NH_4Cl on the reaction over a period of 60 minutes is shown in table 9. In addition to reducing the total color produced, this salt when present in amounts of 3,546.0 p.p.m. Cl or more, causes the fading reaction to begin sooner. However, the degree of fading is apparently no greater than that which occurs in salt-free solutions, which is in contrast to the effect of nitrates.

Summarizing briefly it may be said that the immediate effect of nitrates and sulfates is to increase the color slightly, whereas high chlorides materially decrease the color. Upon standing, nitrates in amounts over 140 p.p.m. cause fading of the blue phosphate color to begin sooner and proceed to a greater degree, the magnitude of this effect depending upon the amount of nitrate present. Other than the initial increase in color, sulfates appear to have no influence on the reaction. Chlorides produce a more immediate but less intense fading than nitrates.

Miscellaneous notes on test

Effect of vanadium. Solutions containing as high as 25 p.p.m. of vanadium as ammonium meta vandate produced no interfering color under the conditions of the determination. Other possible influences of this element have not yet been investigated.

Arsenic. The wide distribution of arsenic in nature, particularly its known presence in certain waters and soils of semiarid regions, its presence in certain phosphate fertilizers, and the possible contamination of plant tissue and soils where arsenicals have been applied as insecticides, emphasize the necessity for being on guard against contamination from this source. As pointed out by Truog and Meyer (2), arsenates are the only compounds of arsenic that interfere. When present, arsenates can be reduced to the trivalent state, which compounds do not interfere with the phosphate determination.

Acidity of final solution. The necessity for maintaining a constant ratio of acid to molybdate should again be emphasized. With a given molybdate concentration too little acid permits some of this constituent to be reduced, giving rise to a blue color, whereas too high an acidity prevents full color development from the ammonium phospho-molybdate present.

Concentration of PO_4 in standard and unknown. The PO_4 concentration of fresh standards should be as near as possible to that of the unknown being tested. The color developed is not strictly proportional to the amount of PO_4 present and serious errors may arise from failure to observe this precaution.

Organic phosphorus. Determination of phosphate in soil extracts colored with organic matter may be inaccurate partly because of the interfering color tints that are developed and the possible interference of such substances on the normal reaction. When such extracts are ignited with $Mg(NO_3)_2$, the determination will then represent both the inorganic and organic phosphorus originally present. However, it is questionable whether the difference between the intensity of the blue color produced by the original solution and that of the oxidized solution should be attributed entirely to organic phosphorus. Inaccuracies in the former determination and the possible presence of inorganic phosphorus in forms other than PO_4 may obviously lead to erroneous conclusions regarding the amounts of organic phosphorus present. Further study on this point is needed.

SUMMARY

Studies on the Truog and Meyer (2) blue colorimetric method for the determination of phosphate have been made. It has been found that stannous chloride solutions, although protected from the air by a layer of mineral oil, nevertheless gradually becomes oxidized. If the reagent is made up in 2-liter quantities, stored in bottles of small cross section, and protected by 1 cm. thick layers of mineral oil, the reagent may be used several months before its deterioration becomes serious.

Under conditions of low acidity, silica may form a silico-molybdate which persists even after the acidity is increased. Upon the addition of stannous chloride this compound undergoes reduction to a blue color indistinguishable from that of the phospho-molybdate. By combining the reagents in a manner favorable to the formation of the silico-molybdate as little as 0.5 p.p.m. SiO_2 may produce an error. On the other hand if the acid and molybdate are combined into one reagent and the test solution is always added to the required amount of this reagent, as much as 700 p.p.m. SiO_2 may be present without appreciable interference.

Ferrous iron in amounts as small as 1 p.p.m. in the final solution diminishes the total color producible if the test solution, after being made to volume (99.5 cc.), is allowed to stand before the addition of stannous chloride. If the reducing agent is added immediately, ferrous iron may be present in large amounts without interfering.

Only in the presence of comparatively high concentrations of nitrates, sulfates, or chlorides, is there any effect upon the accuracy of the test.

When used in accordance with the precautions noted in this paper the Truog and Meyer method combines simplicity, speed, and accuracy, and can be adapted to the determination of phosphorus under a wide range of conditions.

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ON THE ORIGIN OF THE URONIC ACIDS IN THE HUMUS OF SOIL, PEAT, AND COMPOSTS[1]

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The carbohydrates known as hemicelluloses comprise a number of different polysaccharides which give on hydrolysis with hot dilute mineral acids, at atmospheric pressure, not only sugars (hexoses or pentoses or both), but also uronic acids, frequently methoxyl groups and sometimes acetyl groups. Tollens (41) was the first to express the opinion that gums contain d-glucuronic acid. His conclusions were not based upon the isolation of the specific substance, but merely upon certain specific group reactions. Since then, uronic acids have been definitely isolated from a number of the so-called gums, mucilages, pectins, and similar complexes (8, 16, 33), and have been found to be universally distributed in the plant kingdom, as well as to occur also in animal tissues and in microbial cell substance.

The fact is becoming more and more universally recognized that very few hemicelluloses are pure polysaccharides or polymers of only one sugar; on the contrary, most of the preparations so far obtained contain more than one sugar, or mixtures of sugars and uronic acids (25, 18, 21, 24). Before a systematic classification of this group of carbohydrates, based upon the type of sugars and sugar acids produced on hydrolysis, has been developed, all hemicelluloses, gums, mucilages, pectins, and related compounds can be grouped together. This large heterogeneous group of carbohydrates can then be separated into two general subgroups, comprising, (*a*) those complexes that give only sugars, on hydrolysis with dilute mineral acids, or the true hemicelluloses, including hexosans and pentosans; and (*b*) the polyuronides, or those complexes that give, on hydrolysis with mineral acids, uronic acids, in addition to sugars and other compounds, as in the case of the pectins, various gums, etc. (4, 5, 19, 20).

The various methods of analysis of plant tissues for hemicelluloses are based either upon the determination of one group of complexes, such as the pentosans by the furfuraldehyde method, or the several groups, as by hydrolysis with hot dilute mineral acids, after the sugars and starches have been removed. Both of these procedures are far from giving an accurate quantitative determination of the actual content of hemicelluloses. In the first method, which is

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based upon hydrolysis of the pentosan and the subsequent transformation of the pentose to furfuraldehyde,

$$(C_5H_8O_4)n + (n-1)H_2O = n(C_5H_{10}O_5)$$
$$C_5H_{10}O_5 = C_5H_4O_2 + 3\ H_2O$$

Some of the uronic acids will also be determined as pentosans, as shown by the following reaction:

$$C_6H_{10}O_7 = C_5H_{10}O_5 + CO_2$$

In the hydrolysis of hemicelluloses by dilute acids, some of the uronic acids will be destroyed. Heidelberger and Goebel (12) have shown, for example, that when aldobionic acid isolated from pneumococcus is hydrolyzed with 1*N* sulfuric acid for 20 hours, half of the molecule, namely the uronic acid, is largely destroyed. Butler and Cretcher (3) have also found that when aldobionic acid from gum arabic was hydrolyzed with 5 per cent sulfuric acid, d-galactose was obtained while the uronic acid was destroyed to a great extent. According to Weinmann (32), when gum arabic, with a uronic acid content of 17.6 per cent, is hydrolyzed with 2 per cent hydrochloric acid for one and a half hours, enough CO_2 is lost to be equivalent to 12 per cent of the total glucuronic acid of the gum. Link and Niemann (17), using purified uronic acids, have demonstrated that, on boiling with 1*N* sulfuric acid for 15 hours, the acid lost enough CO_2 to be equivalent to 55 per cent of the total glucuronic acid present; when lemon pectin, containing 88 per cent galacturonic acid, was hydrolyzed for 15 hours with 2 per cent sulfuric acid, an equivalent of 33.85 per cent of the acid was liberated as CO_2.

These results as well as others that could be cited (9, 11) are sufficient to illustrate the inaccuracies involved in the quantitative determination of hemicelluloses by the foregoing two procedures. In the method used by the senior author and his associates (37) for the proximate analysis of plant tissues and their decomposition products, such an error was constantly involved. This was fully recognized throughout all the determinations previously published. However, this error was not of such magnitude in the majority of plant substances employed, such as cereal straws, corn stalks, tree products, as to modify the determinations considerably. Since the method was only proximate and since the accounting of 90 to 95 per cent of the plant constituents was the maximum that one could expect under those conditions; it was felt that this method for hemicellulose determination was as good as any other one until a more accurate procedure could be developed; this was especially true because of the fact that the results were always comparable.

However, certain plant substances, such as sphagnum moss, and certain decomposed plant residues, such as peat, and one had a suspicion that it was also true of the humus or the organic matter of the soil itself, always gave a wide discrepancy which was due to the inaccurate determination of the

hemicelluloses. In order to throw light upon this subject, the following investigations were undertaken.

HISTORICAL

With the advance of our knowledge of the complexity of the hemicelluloses, the information concerning the nature and mechanism of their decomposition and synthesis by microörganisms has been rapidly accumulating. It has been established that just as the hemicelluloses vary in their chemical structure, so they vary in the ability of microörganisms to attack them. The fact that a certain fungus or bacterium is capable of decomposing readily one type of hemicellulose is no proof that it will also attack others, frequently even closely related compounds. A marked specificity was found to exist between the chemical structure of these carbohydrates and the ability of microörganisms to attack them (34). This phenomenon is similar in certain respects to the early observations of Pasteur concerning the specificity of certain fungi in attacking the isomers of organic acids.

Some of the hemicelluloses are readily decomposed by a number of bacteria and fungi, as in the case of certain mannans and xylans, whereas others are more resistant to decomposition, especially the various galactans and some of the polyuronides. These phenomena have a direct bearing upon the processes of decomposition of plant and animal residues in soils and in composts and upon the chemical nature of the dark residual material, which is commonly known as humus. Although the plant residues which find their way into the soil are richer in cellulose than in hemicelluloses, the organic matter or humus of the soil itself, as well as of peat and composts, frequently contains no cellulose at all or very little of it, while appreciable quantities of hemicellulose may still be left (38, 35, 39).

A chemical analysis of lowmoor peats has shown that although the plants that contribute to the formation of these types of peat have a much greater percentage of cellulose than of hemicellulose, the peat which results from the anaerobic decomposition of these plants, contains very little cellulose but a considerable quantity of hemicellulose. Only a part of this hemicellulose is found to be pentosan; one lowmoor peat, for example, with 11.03 per cent hemicellulose, as determined by the reducing sugars formed on hydrolysis of the peat with dilute acid, contained only 2.52 per cent pentosan (35). This difference in the rapidity and nature of decomposition of the two types of carbohydrates is due primarily to two factors: *a*. True cellulose is a homogeneous complex and is decomposed completely by microörganisms at a uniform rate, provided the conditions for decomposition are favorable; the hemicelluloses represent a heterogeneous group of substances, some of which are readily attacked by microorganisms and others are more resistant to complete decomposition. *b*. In the process of decomposition of the organic matter by microörganisms, microbial cell substance is constantly synthesized by the organisms bringing about the decomposition processes; this cell substance contains considerable quantities of various hemicelluloses, commonly known as bacterial gums, slimes, capsular material, etc.

Egorov (7) demonstrated in 1911 that when manure undergoes decomposition in compost, the pentosans are attacked more quickly then the cellulose; however, toward the end of the decomposition period, the residual part of the compost contains more pentosan than cellulose. In view of the fact that the pentosan has usually been determined in these investigations by the furfuraldehyde yield obtained on boiling the material with 12 per cent HCl, it is more logical to conclude that, although the content of furfural-yielding substances is lower in the fresh manure than the content of true cellulose and that although those substances underwent a more rapid initial decomposition than the cellulose, there was left in the decomposed or "humified" manure more of the "furfural-yielding substances" than of the cellulose. This is probably a result of at least two distinct processes; the rapid initial decomposition is due to the destruction of the true pentosans, whereas the final accumulation of the resistant complexes is due to the resistance to rapid decomposition of certain uronic acid derivatives which also give furfuraldehyde on boiling with 12 per cent HCl.

Norman (22) has also shown that in the decomposition of straw by a mixture of microorganisms, there was at first a rapid loss of the major part of the hemicelluloses, followed by an equally rapid loss of the cellulose; however, after 12–14 days of decomposition, the hemicelluloses appeared to remain at a certain level, while the cellulose content continued to diminish progressively. This phenomenon was believed to be due to the non-homogeneous nature of the hemicelluloses, differing in the rapidity of their decomposition by microörganisms. The rapid initial loss in hemicelluloses is accompanied by a fall in furfuraldehyde yield, due to loss of the pentose groups. A later increase in these groups may take place, due to the formation of new compounds by the microörganisms; the uronic acid complexes in the straw appeared to be less readily decomposed than the true pentosans.

It is of further interest to note that whereas in the original plant material, the hemicellulose group is usually made up largely of pentosans, especially in the case of cereal straw and other residues, in the soil organic matter the hexosans may predominate over the pentosans.

The determination of pentosans in fresh plant materials, in composts, and in soil is usually based upon the furfuraldehyde yield obtained on boiling the material with 12 per cent HCl; the method of Kröber (14) is commonly employed for this purpose. Because of the fact, however, that uronic acids give on boiling with 12 per cent HCl a pentose and carbon dioxide, it is uncertain how much of the pentosan reported to be present in peat and in soil actually represents the polymer of pentoses and how much is due to the presence of uronic acid complexes in soil. Balks (2) has shown, for example, that although fresh pentosans added to the soil in the form of manures and plant residues decompose readily, the soil organic matter still contains 8.24 to 11.63 per cent pentosan. Methyl pentosans persist in the soil even longer. In general, the pentosan carbon was reported (27, 28) to make up 1.3 to 28.5 per cent of the total organic carbon in soil. Pentosans are especially abundant in peat, although the hydrolysis of peat with dilute acids was found to give, in addition to pentoses, also mannose, galactose, and levulose (10).

Most of the determinations of "pentosan" in soil and in composts probably fall short of the actual amount of total hemicellulose present. Since the pentose units yield only about 75 per cent of the theoretical amount of furfuraldehyde on distillation with mineral acids, since uronic acids give only 33 per cent of their weight as pentose, and further since hemicelluloses contain hexose units also, it is impossible to calculate the total hemicellulose from the determination of "pentosan" by the furfuraldehyde procedure (21).

The presence of uronic acids in soil humus has been recognized only during the last few years. The complexes containing uronic acid are brought into the soil in the form of plant residues and are abundantly synthesized by microörganisms. However, although the uronides in plant residues are made up largely of galacturonic acids, as in the case of fruit pectins, and to a less extent of glucuronic acids, the latter predominate among the microbial products, as in the capsular material of various bacteria.

Shorey and Martin (29) have recently shown that the proportion of uronic acid carbon to the total organic carbon of the soil ranges from 12.8 to 28.4 per cent in the case of mineral soils, and from 5.15 to 9.25 per cent in the case of peats. Only a small part of the uronides in soil will give furfural (12.5 to 35.0 per cent) as determined by the Kröber method, because of incomplete decarboxylation of the uronic acids by this treatment. In the case of peats, the relation between the furfural yield and the theoretical amount calculated from the uronic acid content of the material was 49.0 to 57.5 per cent. However, one should not necessarily consider this as due entirely to the insufficient hydrolysis and carboxylation of the uronic acid complexes. It may also be due to too high a figure obtained by calculating the uronic acid from the CO_2 liberated on hydrolysis. Norman and Martin (23) indicated that in the hydrolysis of pure pectin the CO_2 yield was higher than could be accounted for by the uronic acids present. The analysis of pectin reported in this paper seems to add some weight to this assumption. If this is true of pure pectin, it may certainly hold true of peat and especially of mineral soils, which contain a number of other complexes capable of liberating CO_2 on continued boiling with 12 per cent HCl, even if the carbonates are removed with dilute acid.

In a study of methods for determining the proximate chemical composition of the soil organic matter of soil humus, it was suggested (36) that the hemicellulose content be calculated from the amount of reducing sugar (multiplied by 0.9) obtained by hydrolyzing the soil with hot dilute mineral acids, under ordinary pressure, for several hours. It was found that 5.44 to 12.59 per cent of the total soil organic matter was made up of hemicelluloses. On comparing these results with the amount of pentosan present in the same soils, as determined by the regular furfuraldehyde procedure, it was found that the hemicellulose content obtained by the method of hydrolysis was considerably higher than the pentosan content. As a result of this, it was felt that the reducing sugar liberated from the soil organic matter on hydrolyzing the soil with hot dilute mineral acid at ordinary pressure is a more reliable index of the content of hemicellulose complexes in the soil organic matter than the total pentosan obtained by the furfural method. Because, however, the uronic acid complexes of the soil give reducing sugar on hydrolysis with hot mineral acids, investigations were undertaken, to obtain information which would enable one to correlate the total hemicellulose content of the soil, as measured by the production of reducing sugar, with the amount of uronic acid complexes in the soil organic matter; further, an attempt was also made to throw some light upon the origin of these complexes in the humus of composts and soils, formed under different conditions.

EXPERIMENTAL

In the following investigations, the determination of the total pentosan in the plant material and in soil was carried out according to the method of Kröber (14) as outlined by the Association of Official Agricultural Chemists. For the quantitative measurement of the uronic acids in the organic materials, the procedure of Lefevre and Tollens (15), as modified by Dickson, Otterson, and Link (6) was followed. This method consists in treating the material with an excess of 12 per cent hydrochloric acid, boiling (for 4 hours) until there is no further evolution of carbon dioxide, absorbing this gas in standard barium hydroxide solution, and titrating back with oxalic acid solution. In the case of plant substances, forest organic matter, and peat, 2-gm. portions of dry material were used for each determination, whereas in the case of inorganic soils, 25-gm. portions were employed. The hemicellulose determination was carried out by heating similar quantities of the organic substances with an excess of 2 per cent hydrochloric acid (150–200 cc.) for 5 hours, at ordinary atmospheric pressure, filtering, making up the filtrate to volume, neutralizing the acid, and determining the reducing sugar in an aliquot portion, by the Bertrand method. For the purpose of comparison, the plant substances, peat, and composts were analyzed by the proximate system of analysis, as outlined elsewhere (37).

Purified citrus pectin was employed for the purpose of comparing the three methods of determination of hemicellulose complexes. The following results were obtained:

	per cent
Uronic acid anhydride	76.5
Total furfuraldehyde	18.20
Pentosan equivalent	31.50
Hemicellulose sugar, obtained on boiling for 5 hours with 2 per cent HCl	50.7
Material insoluble on boiling with dilute acid	6.7

According to Norman, uronic acid anhydride gives 16.66 per cent furfuraldehyde. On this basis the furfuraldehyde equivalent of 76.5 per cent uronic acid anhydride would be 12.74 per cent. This leaves 5.46 per cent furfuraldehyde equivalent to 10.63 per cent of free pentose. Whether this free pentose is due to the presence of a free arabinose group in the pectin molecule, as shown by Ehrlich, or to some other factor remains to be determined. The sugar content obtained from the pectin is lower than the theoretical amount calls for, if all the uronic acid is converted by hot dilute acid to reducing sugar in this period of time. However, complete conversion does not take place, because a much longer period of boiling with dilute acid is required for this.

It is interesting to note that Ehrlich (8) reported an average of 72.5 per cent uronic acid in citrus pectin, whereas Dickson, Otterson, and Link reported for purified lemon pectin an equivalent of 72.60 per cent uronic acid anhydride. The reason for the incomplete yield of pentosan and reducing sugar from the uronic acid is to be looked for in the comparatively short period of time allowed for the treatment, and the weak acid used. The important

TABLE 1

Hemicellulose and pentosan content of various "hemicellulose" preparations

On a dry and ash-free basis

SOURCE OF MATERIAL	HEMICELLULOSE CONTENT (REDUCING SUGAR × 0.9)	PENTOSAN CONTENT	URONIC ACID ANHYDRIDE
	per cent	*per cent*	*per cent*
Salep roots	80.8	2.40	1.32
Irish moss	63.0	2.3	1.26
Corn cobs	97.2	101.5	2.80

point to be interpreted from these results is the fact that the hemicellulose sugar content approaches more nearly the actual uronic acid content than the pentosan determination commonly employed in the numerous analyses of plant materials, soils, and composts. In the case of materials, such as gum arabic, with only 15.83 per cent uronic acid anhydride, 80.93 per cent of the material was found as reducing sugar, calculated as glucose, on hydrolysis of the material with dilute acid.

These results lead one to conclude that the sugar produced on hydrolysis of hemicelluloses with dilute acid does not give the theoretical amount of hemicellulose present; the greater the uronic acid content of the material, the greater will be the discrepancy obtained. However, the pentosan figure gives even less approximate results, unless we are dealing with a material that contains pure pentosans. This is shown in table 1. The xylan obtained from corn cobs gave the nearly theoretical amount, whether it was determined by the dilute acid hydrolysis or furfuraldehyde method (34). The preparations from salep roots and from Irish moss consisted largely of mannan and galactan

respectively, and contained only small amounts of pentosan and uronic acids. The corn cob hemicellulose is thus found to represent a practically pure polysaccharide pentosan, giving a hundred per cent sugar on hydrolysis. Anderson (1) also found that corn cob hemicellulose contains only a small amount of uronic acid.

In order to study the fate of hemicelluloses, as measured by the various methods outlined, in the process of decomposition of plant materials by microorganisms, three plant materials were selected, varying distinctly in their nature and chemical composition; namely, oak leaves, rye straw, and sphagnum plants. These materials were available for analysis not only in a fresh state but also in a composted condition, the composts being about 3 years old (30).

TABLE 2

Proximate analysis of fresh and decomposed plant materials, used for pentosan and uronic acid studies

NATURE OF MATERIAL	CONDITIONS OF DECOMPOSITION	PER CENT OF DRY MATERIAL							
		Ether-soluble portion	Alcohol-soluble portion	Cold and hot water-soluble organic matter	Hemicellulose*	Cellulose	Lignin	Crude protein	Ash
Oak leaves.....	Fresh material	3.71	5.92	13.93	12.93	13.78	30.30	4.81	5.09
Oak leaves.....	Decomposed for 3 years	1.65	1.75	8.18	10.24	7.09	36.48	9.38	16.50
Rye straw.....	Fresh material	1.84	3.49	6.26	21.10	38.62	14.63	1.02	4.18
Rye straw.....	Decomposed 3 years, no added nutrients	1.10	1.33	3.24	19.96	27.67	24.88	3.94	8.50
Rye straw.....	Decomposed 3 years, with added nutrient salts	0.84	1.32	7.19	12.54	14.62	26.81	14.18	17.90
Sphagnum.....	Fresh material	1.11	....	6.95	27.73	19.21	7.33	5.50	.....

* Reducing sugar, obtained on boiling material previously treated with hot water, with 2 per cent hydrochloric acid at 100°C. for 5 hours, × 0.9.

In the case of some of the composts, nutrient salts including ammonium compounds and phosphates were originally added, which served to hasten the rapidity and extent of decomposition.

The proximate chemical analyses of the fresh plant materials and of the composts are given in table 2. The results show that with the aerobic decomposition of the plant materials there is a rapid decrease in the water-soluble substances, ether-soluble substances, and cellulose; a slower comparative decrease of the total hemicelluloses; a relative increase of the lignin; and an absolute increase of the protein. By using the increase in ash content as a measure of the extent of decomposition (the composts being kept in pots where no leaching took place), one can readily determine the absolute changes that

have taken place in the concentration of the various chemical constituents of the plant materials as a result of decomposition.

The pentosan, total hemicellulose, and uronic acid figures for these materials are given in table 3. The results throw considerable light upon the comparative value of the different analytical procedures for the determination of the hemicellulose content in plant materials and in composts. In the case of the oak leaves, the total hemicellulose, as determined by hydrolysis of the material with hot dilute mineral acid and measuring the reducing sugars produced, is considerably higher than the pentosan content. The pentosans are

TABLE 3

Uronic acid and pentosan transformations in the decomposition of plant materials by microörganisms

NATURE OF MATERIAL	CONDITIONS OF DECOMPOSITION	PER CENT OF DRY MATERIAL				
		Total pentosan content	Uronic acid anhydride		Hydrolysis of total material by 2 per cent HCl	
			Method of Dickson, Otterson and Link	Method of Shorey and Martin	Total hemicellulose in filtrate (reducing sugar × 0.9)	Pentose sugar in filtrate
Oak leaves	Fresh material	11.70	11.53	9.74	20.10	11.80
Oak leaves	Decomposed for 3 years	7.10	12.30	9.81	10.90	5.50
Rye straw	Fresh material	28.50	4.58	3.59	25.00	22.30
Rye straw	Decomposed 3 years, no added nutrients	20.80	4.03	3.59	22.10	17.90
Rye straw	Decomposed 3 years, with added nutrient salts	10.50	4.61	4.32	14.00	9.20
Sphagnum	Fresh material	11.50	14.54	....	28.60	5.00
Sphagnum	Decomposed 3 years, aerobically	13.55	16.48	....	....	....
Sphagnum	Decomposed 3 years, anaerobically	12.80	15.47	....	....	.....

readily hydrolyzed by hot dilute acids, as shown by the fact that the pentosan in the filtrate is as high as in the total untreated material. The high figure for the uronic acid anhydride content indicates that a large part of the pentosan in the oak leaves is in the form of polyuronides rather than as true pentosans. In the composted oak leaves, the uronic acid figure is higher whereas the pentosan figure is lower, showing that the free pentosans have largely decomposed, accompanied by a relative increase in the concentration of the uronic acid complexes. Table 2 shows that although the quantity of total material, as a result of decomposition, has been reduced to one-third of the initial material (as shown also by the relative ash increase), the cellulose content has dimin-

ished even more rapidly than the total material. The relative concentration of uronic acid has increased in a manner similar to that of the lignin; this tends to indicate that although the uronic acid compounds no doubt undergo a certain amount of decomposition by microorganisms, this process is slower than the decomposition of the cellulose and resembles more that of the lignin.

In the rye straw, the hemicellulose consists predominantly of pentosan. The uronic acid content is very limited, showing that this plant material contains largely the free polysaccharide pentosan. The amount of hemicellulose in the acid hydrolyzate was lower than the total pentosan; this is probably due to a certain loss of some of the pentose sugar during the prolonged boiling of the material with dilute acid, as is also indicated by the lower pentose content of the acid hydrolyzate.

With the decomposition of the rye straw, there is a drop in the total and relative pentosan content, especially in the presence of added nitrogen salts. The relative concentration of the uronic acid compounds, however, was not diminished to any great extent, proving again that this group of complexes undergoes a much slower decomposition than the cellulose and the true pentosans.

Sphagnum represents a type of plant material totally different in nature and chemical composition from the two previously considered. The total hemicellulose content of sphagnum plants was found to be considerably higher than the pentosan content, showing that the material is rich in hemicelluloses of a hexosan nature. The fact that the dilute acid hydrolyzate of the plants contains only about 40 per cent of the total pentosan found in the original plant material in the form of pentose sugar tends to indicate that either there was considerable loss of the pentose in the process of boiling of the material with the dilute acid or that not all the uronic acid complexes give pentoses on treatment with hot dilute mineral acid for a few hours, as brought out previously in the analysis of pectin. Actually the residual material, left after hydrolysis, was found to contain a considerable amount of uronic acid and gave furfuraldehyde on treatment with 12 per cent HCl. Further, the fact that more than 50 per cent of the sphagnum plant, as shown by loss in weight, is hydrolyzed by hot dilute acid and only 28–29 per cent is found as reducing sugar shows that a large part of the material is either volatilized, or not sufficiently hydrolyzed, or changed into non-reducing compounds.

With the advance in decomposition of the sphagnum plants there is no reduction in the uronic acid content but even an actual increase. This is accompanied by a parallel increase in the total pentosan content, tending to bring further evidence to show that most of the furfural obtained by boiling the sphagnum plants with 12 per cent hydrochloric acid is probably derived not from true pentosan but from polyuronides and other complexes.

In order to establish further the rôle of uronic acids in the process of decomposition of plant residues and their transformation into "humus," several peat materials and the organic matter of various horizons of two forest soil profiles

were analyzed. The results are reported in tables 4 and 5. The two peat materials represent a lowmoor peat from Florida (Everglades region) and a highmoor peat from Maine. The lowmoor peat is characterized by practical freedom from cellulose; a very high lignin, protein, and ash content; and a considerable amount of hemicellulose; whereas the highmoor peat contains but little ash and protein, a fair amount of cellulose and lignin, and a considerable amount of hemicellulose.

TABLE 4

Proximate analysis of forest and peat material used for pentosan and uronic acid studies

NATURE OF MATERIAL	DEPTH OR LAYER	PER CENT DRY MATERIAL								
		Ether-soluble portion	Alcohol-soluble portion	Cold and hot water-soluble portion	Hemicellulose	Cellulose	Lignin	Ash	Crude protein	Total accounted for
Lowmoor peat.....	Everglades, Fla., 12–18-inch depth, fibrous layer	3.24	1.34	1.64	8.26	0.43	44.95	6.86	22.75	89.47
Highmoor peat.....	Orono, Maine, upper, younger peat, 1–4-inch depth	2.33	1.72	.....	23.85	14.52	23.16	2.28	4.82	72.68
Surrey spruce.....	Litter	4.72	5.54	.....	15.67	16.31	34.91	3.04	5.81	86.00
Surrey spruce.....	Humus layer	1.67	3.32	.....	9.19	2.36	30.50	26.40	10.44	83.88
White pine needles..	Fresh	6.08	3.34	12.74	20.88†	15.78	31.80	2.74	3.13	86.49
Pine forest soil*....	Litter	6.70	6.10	5.40	20.73†	13.70	35.00	4.00	6.10	‡
Pine forest soil*....	F layer	4.20	4.50	5.10	15.75†	8.20	45.90	13.00	10.60	‡
Pine forest soil*....	H layer	3.90	5.10	4.10	13.45†	5.20	49.50	19.00	11.10	‡
Pine forest soil*....	S H layer (A1)	4.60	4.50	4.70	11.76†	2.60	50.00	75.00	15.00	‡
Pine forest soil*....	Accumulation horizon (B1)	1.00	0.50	2.00	9.09†	1.10	32.30	91.20	36.20	‡

* Analyses of these materials reported on an ash-free basis.

† These analyses were made on separate portions of the fresh material.

‡ No total can be reported for these, since, in order to illustrate the changes in the organic matter content and because of the high ash content of the lower layers, the calculations were made on the ash-free material of this profile.

The relative concentration of total hemicellulose, pentosan, and uronic acid in these two peats is given in table 5. These results show that, in the case of the lowmoor peat, the amounts of pentosan and hemicellulose sugar produced on hydrolysis with dilute acids are not higher than the uronic acid content of the peat; provided all the uronic acid is hydrolyzed in that period of time to give reducing sugar, the peat is found to contain very little free pentosan but a certain amount of hexosan hemicelluloses.

The highmoor peat was found to contain a considerably larger amount of hemicellulose than of pentosan and uronic acid, showing that this material is rich in hexosan hemicelluloses. The fact that the amount of uronic acid found in this peat is considerable makes the presence of free pentosan in this material highly problematical, a fact already emphasized for sphagnum plants. Since certain polyuronides, as the citrus pectin, yield on hydrolysis with dilute acids only a part of the pentose that one might expect from theoretical calculations, one may be justified in concluding that the high uronic acid content of the sphagnum peat is sufficient evidence of the presence of substances not ac-

TABLE 5

Uronic acid and pentosan content of humus in peat and forest soils

NATURE OF MATERIAL	DEPTH OR LAYER	PER CENT OF DRY MATERIAL				
			Uronic acid anhydride		Hydrolysis by 2 per cent HCl	
		Total pentosan	Method of Dickson, Otterson and Link	Method of Shorey and Martin	Hemicellulose in filtrate	Pentosan in filtrate
Lowmoor peat.....	Everglades, Fla., 12–18-inch depth, fibrous layer	6.6	9.66	6.96	9.2	5.1
Highmoor peat.....	Orono, Maine, upper, younger peat, 1–4-foot depth	11.9	15.63	12.08	26.60	9.7
Surrey spruce.....	Litter	7.5	5.89	5.05	16.90	6.0
Surrey spruce.....	Humus layer	3.8	10.98	(5.64)?	9.60	2.9
White pine needles.....	Fresh	8.5	6.35	.....	20.88	...
Pine forest soil*.....	Litter	9.79	6.96	.....	20.73	...
Pine forest soil*.....	F layer	7.59	7.69	.....	15.75	...
Pine forest soil*.....	H layer	5.74	7.56	.....	13.45	...
Pine forest soil*.....	S H layer (A1)	4.48	9.20	.....	11.76	...
Pine forest soil*.....	Accumulation horizon (B1)	2.27	32.39	.....	9.09	...

* Analyses of these materials are reported on an ash-free basis.

counted for in the proximate analysis of this peat (35). It is of considerable interest to note that, although the total hemicellulose is somewhat lower in the sphagnum peat than in fresh sphagnum plants, the uronic acid content is higher, bearing out the same general principle observed previously that, with the advance of decomposition of plant material, there is a decrease in the total hemicellulose content but a relatively smaller decrease of the uronic acid complexes.

In this connection, it may be of interest to call attention to the results of Keppeler (13), concerning the ratio of hexosan to pentosan in different peat

materials of different age (taken from different depths of peat bogs). It was found that with the advance of decomposition of peat there is an increase in the hexosan-pentosan ratio, namely, from an average of 2.95:1, in the case of young sphagnum peat, to 4.1:1, in the case of old sphagnum peat. Although Keppeler included also the true cellulose among the hexosans, the fact that the cellulose is decomposed very readily and is found in diminishing amounts with an increase in age of peat would lead us to conclude that the increase in the hexosan-pentosan ratio is due to a more rapid destruction of the pentosans than of the hexosan hemicelluloses and uronic acid complexes.

One of the two forest soil profiles[2] was taken from an undisturbed forest soil at Keene, N. H., and one represents a Surrey spruce soil; of the latter, only the two organic matter layers above the inorganic soil were available. The proximate analysis of the various horizons of these soil profiles and the corresponding hemicellulose determinations are reported in tables 4 and 5. With the advance in the decomposition of the forest residues, there is a rapid decrease in the relative cellulose content and an increase in the ash, protein, and lignin content. The marked increase in protein in the accumulation horizon is due probably to the fact that the protein is washed down more readily than the non-nitrogenous complexes, a phenomenon already emphasized by Weis (40).

As to the changes in the relative concentration of the different hemicelluloses with the advance in decomposition of the organic matter, we find a rapid decrease in the total pentosan, a smaller decrease in the total hemicellulose content, and an actual relative increase in the uronic acid content. The exact quantitative relationship between the pentosan, total hemicellulose, and uronic acid content of different plant materials and especially of the various decomposition products is not fully known, because of the fact that the hydrolysis of uronic acid complexes does not give under these conditions the theoretical amount of reducing sugar and because different uronides contain different amounts of pentose sugar; a knowledge of the relative transformation of these three types of hemicellulose; namely, the total pentosan, the total hemicellulose, as measured by the amount of reducing sugar formed on hydrolysis of the material with hot dilute mineral acids, and the uronic acid content, enables us to interpret the behavior of these complexes in the process of decomposition of organic matter in the soil. The results so far obtained point definitely to the fact that although some hemicelluloses, especially the true pentosans, undergo rapid decomposition, other hemicelluloses, especially certain uronic acid complexes, decompose much more slowly. As a result of this, the total hemicellulose content may sometimes diminish rapidly in the process of decomposition of the plant materials in soils and in composts, as in the case of the rye straw, which is rich in true pentosans; at other times, the total hemicellulose may diminish very slowly, as in the case of the sphagnum

[2] The authors are indebted to Dr. Watson of this laboratory for collecting this material.

plants rich in polyuronides; in still other cases, the hemicellulose transformation is irregular, as in the case of different forest materials, because of their varying chemical composition. This is the reason why different fungi and bacteria were found (26, 31) to decompose pentosans in different plant materials at a different rate, no doubt because of the different chemical nature of the "pentosans" in these plant materials.

For the determination of uronic acids, the method of Shorey and Martin was compared, in some instances, with that of Dickson, Otterson, and Link. The first method gave invariably lower results, with undecomposed plant material, peat, and forest soils. This is because this method calls for boiling the material for one hour with 200 cc. of 1 per cent hydrochloric acid, in order to remove the carbonates. The fact that by this procedure, a considerably lower uronic acid content was obtained in the case of highmoor peat which has a pH of 4.0 and is practically free from carbonates shows that some loss of uronic acid-CO_2 takes place in the procedure recommended by Shorey and

TABLE 6

Pentosan and uronic acid content in soil organic matter

NUMBER OF SOIL	TREATMENT OF SOIL	CARBON CONTENT OF SOIL	ORGANIC MATTER IN SOIL	TOTAL PENTOSAN IN SOIL ORGANIC MATTER	HEMICELLULOSE IN SOIL ORGANIC MATTER (HYDROLYSIS BY 2 PER CENT HCl	URONIC ACID ANHYDRIDE IN SOIL ORGANIC MATTER	URONIC ACID CARBON, PERCENTAGE OF TOTAL ORGANIC CARBON
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	
5A	Manured	1.45	2.49	8.35	10.40	19.23	13.56
7A	Untreated	0.76	1.31	4.58	5.80	31.65	23.16
5B	Manured and limed	1.75	3.01	5.25	7.71	12.87	9.09
7B	Limed only	1.06	1.82	4.06	5.33	19.98	14.06

Martin. Hence the original method of Dickson et al., was employed in most other determinations.

In order to establish further the relationship between the different hemicelluloses in humus of inorganic soils, which contain only a small amount of organic matter, a series of plots of a Sassafrass soil, variously treated for the last 20 years, were selected. As a result of the treatment of these soils with stable manure and lime, accompanied by cultivation and yearly crop growth, their organic matter content has become markedly modified both in quantity and kind. The plot receiving stable manure year after year (5A) contains nearly twice as much total organic matter as the unfertilized plot (7A). The plot receiving lime only contains more carbon than the untreated plot, because of the better crop growth and, therefore, of the larger amounts of plant residues left year after year in the soil. Liming of the soil resulted in a much greater reduction of the pentosan than of the total hemicellulose; although the limed soils contain more total organic matter than the corresponding unlimed soils,

they contain less pentosan. The limed soils also contain less total hemicellulose and less of the uronic acid complexes, showing that the effect of lime upon the soil makes conditions favorable for the microorganisms capable of decomposing the more resistant hemicelluloses.

The fact that the uronic acid complexes are more resistant to rapid decomposition than cellulose and the true pentosans is brought out from the uronic acid figures. The unmanured plots were found to contain a much greater relative concentration of uronic acid complexes than the manured plots, this being true for both the limed and unlimed plots. In fact, nearly an inverse ratio was found to exist between the total amount of organic matter and the uronic acid content. The ratio for the total organic matter of the two unlimed plots (5A:7A) is equal to 1.9:1; the inverse ratio between the uronic acid content of the organic matter of these two plots is 1.7:1. The ratio of the organic matter content of the two limed plots (5B:7B) is equal to 1.65:1; the inverse ratio between the uronic acid content of these two plots is 1.55:1. This points further to the greater resistance to decomposition of the uronic acid complexes than of the other chemical constituents in plant residues; as a result of this, these complexes contribute an important fraction to the humus of the soil.

A knowledge of the relation between the different hemicelluloses is thus found to be of great importance not only for our understanding of the processes of decomposition of plant residues in composts, in peat, and in soil, but also for our understanding of the chemical nature of the humus of the soil. However, in attempting to measure these hemicelluloses quantitatively, at least four factors must be considered: *a*. In hydrolyzing the organic matter with mineral acids, incomplete transformation into sugar may take place, especially in the case of the uronic acid complexes, unless the boiling is prolonged. *b*. Under these conditions, some of the sugar may be destroyed or changed to furfural. *c*. The CO_2 obtained on boiling soil or peat with mineral acids may not come entirely from uronic acids, but from other organic and inorganic complexes. *d*. The hemicelluloses in soil humus, being made up of hexoses, pentoses, uronic acids, and possibly other groups, cannot possibly be measured by one single method; any one method will give only an imperfect idea of the abundance of the hemicelluloses.

SUMMARY

Under the term "hemicellulose," the authors include both the true hemicelluloses, as conceived originally by Schulze, and the polyuronides, according to the more recent conceptions of complexes which consist of mixtures of sugars and uronic acids.

In this paper a series of analyses are presented giving the abundance of pentosans, of total hemicelluloses, and of uronic acid complexes in plant materials, in composts where plant substances are undergoing active decomposition, in peats, in forest soils, and in mineral soils.

The results obtained show that in the decomposition of plant residues, the

true pentosans are attacked more rapidly by microorganisms than are the uronic acid complexes. Whether these are as such more resistant to decomposition or whether they form compounds with the other chemical complexes as lignins and proteins, which renders them more resistant to rapid decomposition, still remains to be determined.

Different plant materials vary in the relative concentration of the different hemicelluloses and in the relative rapidity with which these are decomposed by microorganisms.

With the advance of decomposition of plant residues, there is a progressive diminution of the pentosans and a relative increase of the uronic acid complexes.

Manuring of soil results in an increase in the pentosan content, whereas continued cultivation of soil without the addition of fresh organic manures or plant residues, results in a rapid reduction of the total soil humus and a corresponding relative increase in uronic acid complexes.

The nature of the soil, its reaction, soil treatment, and system of fertilization will all modify not only the abundance of the total organic matter in soil, but also its chemical composition.

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